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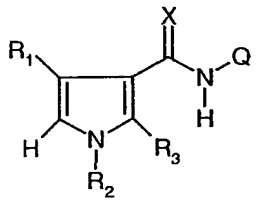
(54) Title: PYRROLCARBOXAMIDES AND PYRROLCARBOTHIOAMIDES AND THEIR AGROCHEMICAL USES

(57) Abstract: The invention relates to novel pesticidal pyrrolcarboxamide of the formula (I), wherein X is oxygen or sulfur; R_1 is CF_3, CF_2H or CFH_2; R_2 is C_1-C_3alkyl, C_1-C_3haloalkyl, C_1-C_3alkoxy-C_1-C_3alkyl or C_1-C_3haloalkoxy-C_1-C_3alkyl; R_3 is hydrogen, methyl, CF_3 or fluoro; Q is (Q1), (Q2), (Q3), (Q4); R_4 is C_6-C_{14}bicycloalkyl unsubstituted or substituted by methyl, ethyl or CF_3; C_6-C_{14}bicycloalkenyl unsubstituted or substituted by methyl, ethyl or CF_3; C_6-C_{14}bicycloalkadienyl unsubstituted or substituted by methyl, ethyl or CF_3; a group of the form (a) wherein R_7, R_8, R_9 are independently of each other C_1-C_3alkyl or C_1-C_3haloalkyl; or a group (b) wherin R_{10} and R_{11} are independently of each other hydrogen or halogen and n=1 or 2; and R_5 and R_6 are independently of each other hydrogen or halogen. The novel compounds have plant-protecting properties and are suitable for protecting plants against infestation by phytopathogenic microorganisms.

PYRROLCARBOXYAMIDES AND PYRROLCARBOTHIOAMIDES AND THEIR AGROCHEMICAL USES

The present invention relates to novel pyrrolecarboxylic acid amides and pyrrolecarbothioic acid amides which have microbicidal activity, in particular fungicidal activity. The invention also relates to the preparation of these substances, to agrochemical compositions which comprise at least one of the novel compounds as active ingredient, to the preparation of the compositions mentioned and to the use of the active ingredients or compositions in agriculture and horticulture for controlling or preventing infestation of plants by phytopathogenic microorganisms, preferably fungi.

The 3-pyrrolecarboxylic acid amides and 3-pyrrolecarbothioic acid amides of the present invention have the general formula (I),



I

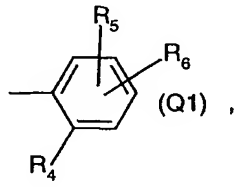
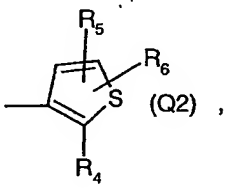
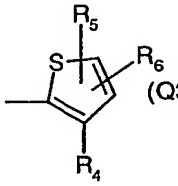
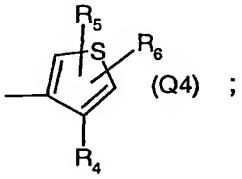
wherein

X is oxygen or sulfur;

R_1 is CF_3, CF_2H or CFH_2;

R_2 is C_1-C_3alkyl, C_1-C_3haloalkyl, C_1-C_3alkoxy-C_1-C_3alkyl or C_1-C_3haloalkoxy-C_1-C_3alkyl;

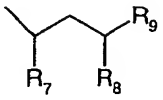
R_3 is hydrogen, methyl, CF_3 or fluoro;

Q is  (Q1),  (Q2),  (Q3),  (Q4);

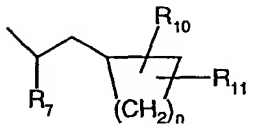
R_4 is C_6-C_{14}bicycloalkyl unsubstituted or substituted by methyl, ethyl or CF_3;

C_6-C_{14}bicycloalkenyl unsubstituted or substituted by methyl, ethyl or CF_3;

C_6-C_{14}bicycloalkadienyl unsubstituted or substituted by methyl, ethyl or CF_3; or a group of the form



wherein R_7, R_8 and R_9 are independently of each other C_1-C_3alkyl or C_1-C_3haloalkyl; or a group



wherein R_{10} and R_{11} are independently of each other hydrogen or halogen and n = 1 or 2; and

R_5 and R_6 are independently of each other hydrogen or halogen.

Surprisingly, it has now been found that the compounds of formula I exhibit improved biological properties which render them more suitable for the practical use in agriculture and horticulture.

Where asymmetrical carbon atoms are present in the compounds of formula I, these compounds are in optically active form. The invention relates to the pure isomers, such as enantiomers and diastereomers, as well as to all possible mixtures of isomers, e.g. mixtures of diastereomers, racemates or mixture of racemates.

Within the present specification alkyl denotes methyl, ethyl, n-propyl and isopropyl. Non-branched alkyl is preferred. Alkyl as part of other radicals such as alkoxy, haloalkyl, etc. is understood in an analogous way. Halogen will be understood generally as meaning fluoro, chloro, bromo or iodo. Fluoro, chloro or bromo are preferred meanings. Halogen as part of other radicals such as haloalkyl, haloalkoxy, etc. is understood in an analogous way.

Bicycloalkyl is, depending on the ring size, bicyclo[2.1.1]hexane, bicyclo[2.2.1]heptane, bicyclo[2.2.2]octane, bicyclo[3.2.1]octane, bicyclo[3.2.2]nonane, bicyclo[4.2.2]decane, bicyclo[4.3.2]undecane, adamantane and the like.
Bicycloalkenyl is bicyclo[2.1.1]hex-4-ene, bicyclo[2.2.1]hept-2-ene, bicyclo[2.2.2]oct-2-ene and the like.
Bicycloalkadienyl is bicyclo[2.2.1]hepta-2,5-diene, bicyclo[2.2.2]octa-2,5-diene, and the like.

One specific subgroup of the compounds of formula I is the group wherein X is oxygen.

Another specific subgroup of the compounds of formula I is the group wherein X is sulfur.

Preferred subgroups of compounds of formula I are those wherein

X is oxygen; or

X is sulfur; or

R_1 is CF_3; or

R_1 is CF_2H; or

R_1 is CFH_2; or

R_2 is C_1-C_3alkyl; or

R_2 is C_1-C_3haloalkyl; or

R_2 is C_1-C_3alkoxy-C_1-C_3alkyl; or

R_2 is C_1-C_3haloalkoxy-C_1-C_3alkyl; or

R_2 is C_1-C_3alkyl or C_1-C_3haloalkyl; or

R_2 is C_1-C_3alkyl, C_1-C_3haloalkyl or C_1-C_3alkoxy-C_1-C_3alkyl; or

R_2 is methyl or CH_2OCH_3; or

R_2 is methyl; or

R_3 is hydrogen; or

R_3 is methyl; or

R_3 is CF_3; or

R_3 is fluoro; or

R_3 is hydrogen or fluoro; or

Q is Q1; or

Q is Q2, Q3 or Q4; or

Q is Q2; or

Q is Q3; or

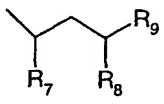
Q is Q4; or

R_4 is C_6-C_{10}bicycloalkyl unsubstituted or substituted by methyl, ethyl or CF_3; or

C_6-C_{10}bicycloalkenyl unsubstituted or substituted by methyl, ethyl or CF_3; or

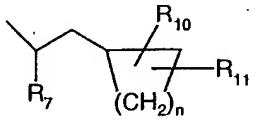
C_6-C_{10}bicycloalkadienyl unsubstituted or substituted by methyl, ethyl or CF_3; or

a group of the form



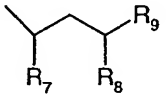
wherein R_7, R_8 and R_9 are independently of each other C_1-C_3alkyl or

C_1-C_3haloalkyl; or a group



wherein R_{10} and R_{11} are independently of each other hydrogen or halogen and n = 1 or 2; or

R_4 is C_6-C_{10}bicycloalkyl unsubstituted or substituted by methyl, ethyl or CF_3 , C_6-C_{10}bicycloalkenyl unsubstituted or substituted by methyl, ethyl or CF_3 , C_6-C_{10}bicycloalkadienyl unsubstituted or substituted by methyl, ethyl or CF_3 , or a group of the form



wherein R_7, R_8 and R_9 are independently of each other C_1-C_3alkyl or C_1-C_3haloalkyl; and

R_5 and R_6 are independently of each other hydrogen, chloro, bromo or fluoro; or

R_5 and R_6 are independently of each other hydrogen, chloro or fluoro; or

R_5 is hydrogen and R_6 is chloro or fluoro.

Further preferred subgroups are those wherein

a) X is oxygen;

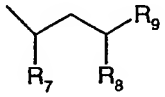
R_1 is CF_3;

R_2 is C_1-C_3alkyl or C_1-C_3alkoxy-C_1-C_3alkyl;

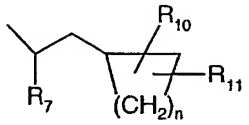
R_3 is hydrogen or fluoro;

Q is Q1;

R_4 is C_6-C_{10}bicycloalkyl unsubstituted or substituted by methyl, ethyl or CF_3; or C_6-C_{10}bicycloalkenyl unsubstituted or substituted by methyl, ethyl or CF_3 ; or C_6-C_{10}bicycloalkadienyl unsubstituted or substituted by methyl, ethyl or CF_3 ; or a group of the form



wherein R_7, R_8 and R_9 are independently of each other C_1-C_3alkyl or C_1-C_3haloalkyl; or a group



wherein R_{10} and R_{11} are independently of each other hydrogen or halogen and n = 1 or 2; and

R_5 and R_6 are independently of each other hydrogen, fluoro, chloro or bromo; or

b) X is oxygen;

R_1 is CF_3;

R_2 is C_1-C_3alkyl or C_1-C_3haloalkyl;

R_3 is hydrogen or fluoro;

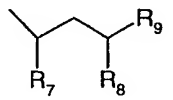
Q is Q2, Q3 or Q4;

R_4 is C_6-C_{10}bicycloalkyl unsubstituted or substituted by methyl, ethyl or CF_3; or

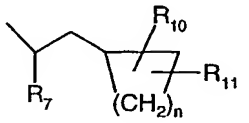
C_6-C_{10}bicycloalkenyl unsubstituted or substituted by methyl, ethyl or CF_3; or

C_6-C_{10}bicycloalkadienyl unsubstituted or substituted by methyl, ethyl or CF_3; or

a group of the form



wherein R_7, R_8 and R_9 are independently of each other C_1-C_3alkyl or C_1-C_3haloalkyl; or a group



wherein R_{10} and R_{11} are independently of each other hydrogen or halogen and n = 1 or 2; and

R_5 and R_6 are independently of each other hydrogen, fluoro, chloro or bromo; and among this subgroup Q = Q2 is preferred; or

ab) X is oxygen;

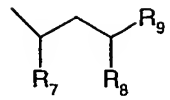
R_1 is CF_3;

R_2 is methyl or CH_2OCH_3;

R_3 is hydrogen or fluoro;

Q is Q1;

R_4 is a group of the form



wherein R_7, R_8 and R_9 are independently of each other C_1-C_3alkyl or C_1-C_3haloalkyl; and

R_5 and R_6 are independently of each other hydrogen, fluoro, chloro or bromo; or

c) X is oxygen;

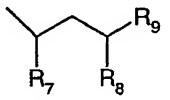
R_1 is CF_3;

R_2 is methyl;

R_3 is hydrogen or fluoro;

Q is Q1;

R_4 is a group of the form



wherein R_7, R_8 and R_9 are independently of each other CF_3, methyl or ethyl, preferably methyl; and

R_5 and R_6 are independently of each other hydrogen, fluoro or chloro; or

d) X is oxygen;

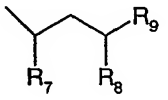
R_1 is CF_3;

R_2 is methyl;

R_3 is hydrogen;

Q is Q1;

R_4 is a group of the form



wherein R_7, R_8 and R_9 are independently of each other methyl or ethyl, preferably methyl; and

R_5 and R_6 are independently of each other hydrogen, fluoro or chloro; or

e) X is oxygen;

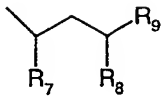
R_1 is CF_3;

R_2 is methyl;

R_3 is fluoro;

Q is Q1;

R_4 is a group of the form

 wherein R_7, R_8 and R_9 are independently of each other methyl or ethyl,

preferably methyl; and

R_5 and R_6 are independently of each other hydrogen, fluoro or chloro.

Other preferred subgroups are those wherein

f) X is sulfur;

R_1 is CF_3;

R_2 is C_1-C_3alkyl or C_1-C_3haloalkyl;

R_3 is hydrogen or fluoro;

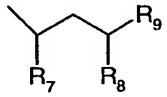
Q is Q1;

R_4 is C_6-C_{10}bicycloalkyl unsubstituted or substituted by methyl, ethyl or CF_3; or

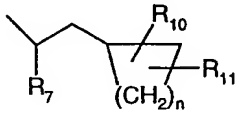
C_6-C_{10}bicycloalkenyl unsubstituted or substituted by methyl, ethyl or CF_3; or

C_6-C_{10}bicycloalkadienyl unsubstituted or substituted by methyl, ethyl or CF_3; or

a group of the form

 wherein R_7, R_8 and R_9 are independently of each other C_1-C_3alkyl or

C_1-C_3haloalkyl; or a group

 wherein R_{10} and R_{11} are independently of each other hydrogen or

halogen and n = 1 or 2; and

R_5 and R_6 are independently of each other hydrogen, fluoro, chloro or bromo; or

g) X is sulfur;

R_1 is CF_3;

R_2 is C_1-C_3alkyl or C_1-C_3haloalkyl;

R_3 is hydrogen or fluoro;

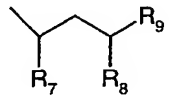
Q is Q2, Q3 or Q4;

R_4 is C_6-C_{10}bicycloalkyl unsubstituted or substituted by methyl, ethyl or CF_3; or

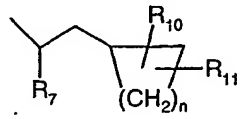
C_6-C_{10}bicycloalkenyl unsubstituted or substituted by methyl, ethyl or CF_3; or

C_6-C_{10}bicycloalkadienyl unsubstituted or substituted by methyl, ethyl or CF_3; or

a group of the form

 wherein R_7, R_8 and R_9 are independently of each other C_1-C_3alkyl or

C_1-C_3haloalkyl; or a group

 wherein R_{10} and R_{11} are independently of each other hydrogen or

halogen and n = 1 or 2; and

R_5 and R_6 are independently of each other hydrogen, fluoro, chloro or bromo.

Other subgroups of compounds of formula I are those wherein

h) X is oxygen or sulfur;

R_1 is CF_3;

R_2 is C_1-C_3alkyl, C_1-C_3haloalkyl or C_1-C_3alkoxy-C_1-C_3alkyl ;

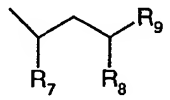
R_3 is hydrogen or fluoro;

Q is Q1;

R_4 is C_6-C_{10}bicycloalkyl unsubstituted or substituted by methyl, ethyl or CF_3;

C_6-C_{10}bicycloalkenyl unsubstituted or substituted by methyl, ethyl or CF_3;

C_6-C_{10}bicycloalkadienyl unsubstituted or substituted by methyl, ethyl or CF_3; a group of the form

 wherein R_7, R_8 and R_9 are independently of each other C_1-C_3alkyl or

C_1-C_3haloalkyl; and

R_5 and R_6 are independently of each other hydrogen, chloro or fluoro; or

i) X is oxygen or sulfur;

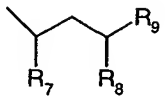
R_1 is CF_3;

R_2 is C_1-C_3alkyl, C_1-C_3haloalkyl or C_1-C_3alkoxy-C_1-C_3alkyl ;

R_3 is hydrogen or fluoro;

Q is Q1;

R_4 is a group of the form



wherein R_7, R_8 and R_9 are independently of each other C_1-C_3alkyl or

C_1-C_3haloalkyl; and

R_5 and R_6 are independently of each other hydrogen, chloro or fluoro; or

j) X is oxygen or sulfur;

R_1 is CF_3;

R_2 is C_1-C_3alkyl, C_1-C_3haloalkyl or C_1-C_3alkoxy-C_1-C_3alkyl;

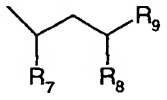
R_3 is hydrogen or fluoro;

Q is Q2, Q3 or Q4;

R_4 is C_6-C_{10}bicycloalkyl unsubstituted or substituted by methyl, ethyl or CF_3;

C_6-C_{10}bicycloalkenyl unsubstituted or substituted by methyl, ethyl or CF_3;

C_6-C_{10}bicycloalkadienyl unsubstituted or substituted by methyl, ethyl or CF_3; a group of the form



wherein R_7, R_8 and R_9 are independently of each other C_1-C_3alkyl or

C_1-C_3haloalkyl; and

R_5 and R_6 are independently of each other hydrogen, chloro or fluoro; or

k) X is oxygen or sulfur;

R_1 is CF_3;

R_2 is C_1-C_3alkyl, C_1-C_3haloalkyl or C_1-C_3alkoxy-C_1-C_3alkyl;

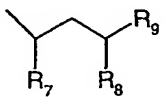
R_3 is hydrogen or fluoro;

Q is Q2;

R_4 is C_6-C_{10}bicycloalkyl unsubstituted or substituted by methyl, ethyl or CF_3;

C_6-C_{10}bicycloalkenyl unsubstituted or substituted by methyl, ethyl or CF_3;

C_6-C_{10}bicycloalkadienyl unsubstituted or substituted by methyl, ethyl or CF_3; a group of the form



wherein R_7, R_8 and R_9 are independently of each other C_1-C_3alkyl or

C_1-C_3haloalkyl; and

R_5 and R_6 are independently of each other hydrogen, chloro or fluoro; or

l) X is oxygen or sulfur;

R_1 is CH_2F or CF_2H;

R_2 is C_1-C_3alkyl, C_1-C_3haloalkyl or C_1-C_3alkoxy-C_1-C_3alkyl;

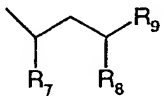
R_3 is hydrogen or fluoro;

Q is Q1;

R_4 is C_6-C_{10}bicycloalkyl unsubstituted or substituted by methyl, ethyl or CF_3;

C_6-C_{10}bicycloalkenyl unsubstituted or substituted by methyl, ethyl or CF_3;

C_6-C_{10}bicycloalkadienyl unsubstituted or substituted by methyl, ethyl or CF_3; a group of the form



wherein R_7, R_8 and R_9 are independently of each other C_1-C_3alkyl or C_1-C_3haloalkyl; and

R_5 and R_6 are independently of each other hydrogen, chloro or fluoro; or

m) X is oxygen;

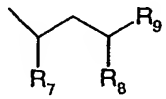
R_1 is CH_2F or CF_2H;

R_2 is methyl or CH_2OCH_3;

R_3 is hydrogen or fluoro;

Q is Q1;

R_4 is a group of the form



wherein R_7, R_8 and R_9 are independently of each other C_1-C_3alkyl or C_1-C_3haloalkyl; and

R_5 and R_6 are independently of each other hydrogen, chloro or fluoro; or

n) X is oxygen or sulfur;

R_1 is CH_2F or CF_2H;

R_2 is C_1-C_3alkyl, C_1-C_3haloalkyl or C_1-C_3alkoxy-C_1-C_3alkyl;

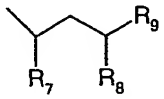
R_3 is hydrogen or fluoro;

Q is Q2, Q3 or Q4;

R_4 is C_6-C_{10}bicycloalkyl unsubstituted or substituted by methyl, ethyl or CF_3;

C_6-C_{10}bicycloalkenyl unsubstituted or substituted by methyl, ethyl or CF_3;

C_6-C_{10}bicycloalkadienyl unsubstituted or substituted by methyl, ethyl or CF_3; a group of the form



wherein R_7, R_8 and R_9 are independently of each other C_1-C_3alkyl or C_1-C_3haloalkyl; and

R_5 and R_6 are independently of each other hydrogen, chloro or fluoro; or

o) X is oxygen;

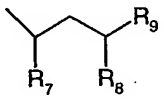
R_1 is CH_2F or CF_2H;

R_2 is methyl or CH_2OCH_3;

R_3 is hydrogen or fluoro;

Q is Q2, Q3 or Q4;

R_4 is a group of the form



wherein R_7, R_8 and R_9 are independently of each other C_1-C_3alkyl or C_1-C_3haloalkyl; and

R_5 and R_6 are independently of each other hydrogen, chloro or fluoro.

Preferred individual compounds are :

1-methyl-4-trifluoromethyl-1H-pyrrole-3-carboxylic acid [2-(1,3-dimethylbutyl)phenyl]amide;

1-methoxymethyl-4-trifluoromethyl-1H-pyrrole-3-carboxylic acid [2-(1,3-dimethylbutyl)phenyl]amide;

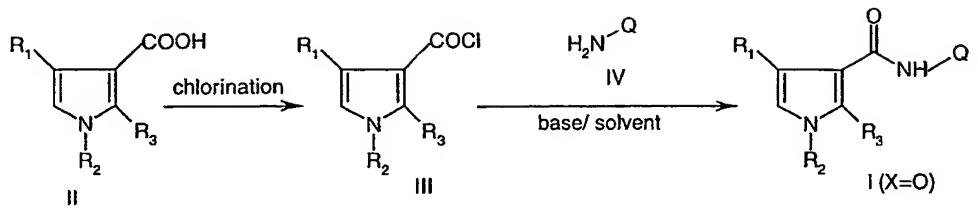
1-methyl-2-fluoro-4-trifluoromethyl-1H-pyrrole-3-carboxylic acid [2-(1,3-dimethylbutyl)phenyl]amide;

1-methoxymethyl-2-fluoro-4-trifluoromethyl-1H-pyrrole-3-carboxylic acid [2-(1,3-dimethylbutyl)phenyl]amide;

1-methyl-4-trifluoromethyl-1H-pyrrole-3-carbothioic acid [2-(1,3-dimethylbutyl)phenyl] amide.

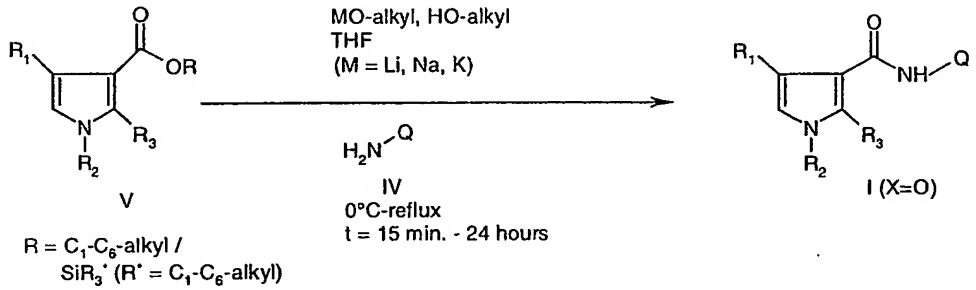
The compounds according to formula I wherein X is oxygen may be prepared according to the following reaction Scheme 1A.

Scheme 1A



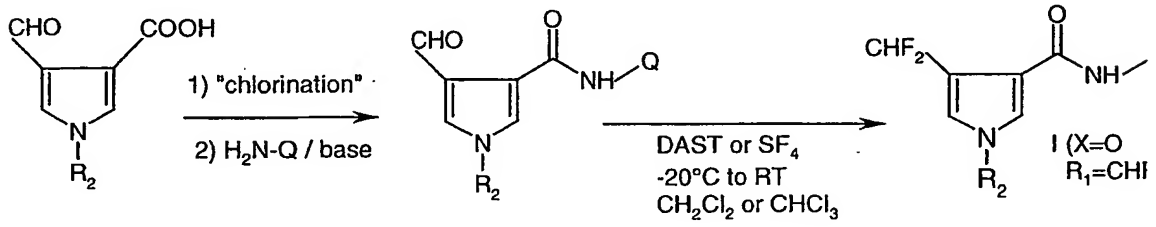
The compounds of the formula I wherein X is oxygen may also be prepared from the corresponding esters according to reaction Scheme 1B.

Scheme 1B



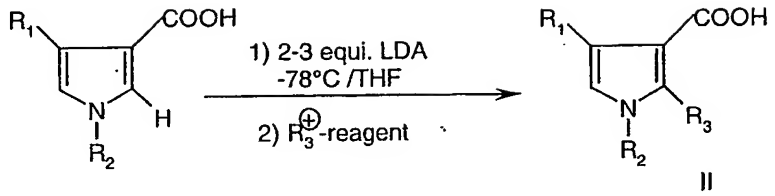
A further method for the synthesis of compounds of the formula I is outlined in Scheme 1C.

Scheme 1C



The synthesis of the pyrrole carboxylic acids of formula II wherein R_3 is not hydrogen may be conducted according to Scheme 2A.

Scheme 2A



II

$R_3^{\oplus}$-reagents : $F^{\oplus}$= N-fluoro-bis(phenylsulfonyl)amine, N-fluoro-N-methyl-toluene-4-sulfonamide, 2-fluoro-3,3-dimethyl-2,3-dihydro-1,2-benzisothiazole-1,1-dioxide, 1-fluoro-sym.-collidiniumtetrafluoroborate

$Me^{\oplus}$= MeI, MeBr, DMS (dimethylsulfate)

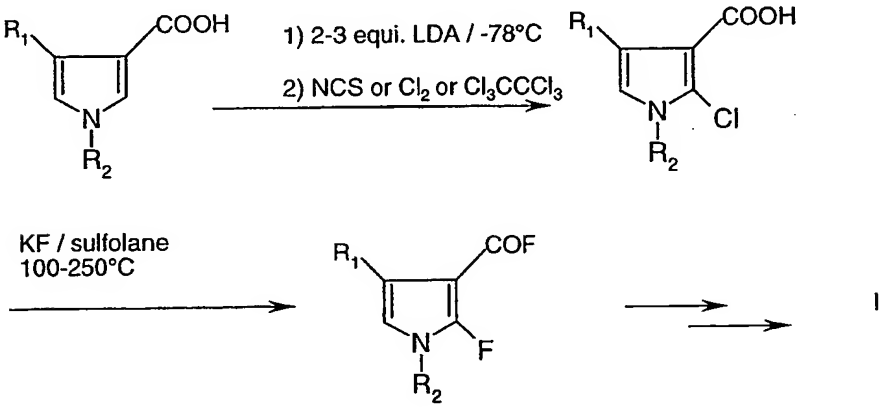
$Cl^{\oplus}$= NCS, Cl_2, hexachloroethane

LDA = lithiumdiisopropylamide

The synthesis of the pyrrole carboxylic acids of formula II wherein R_3 = H is described in WO-00/09482.

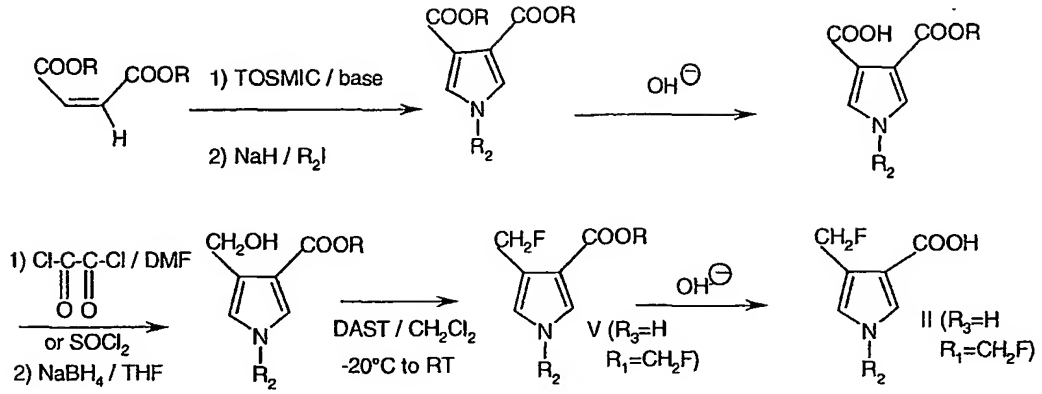
Alternatively the pyrrole carboxylic acid fluorides wherein R_3 is fluoro may be obtained as outlined in Scheme 2B.

Scheme 2B

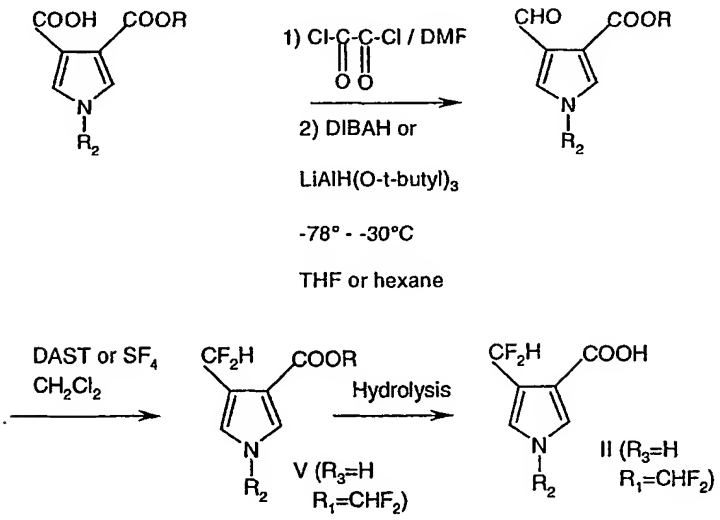


The synthesis of the pyrrole carboxylic acids II may also be conducted according to the Schemes 2C or 2D.

Scheme 2C



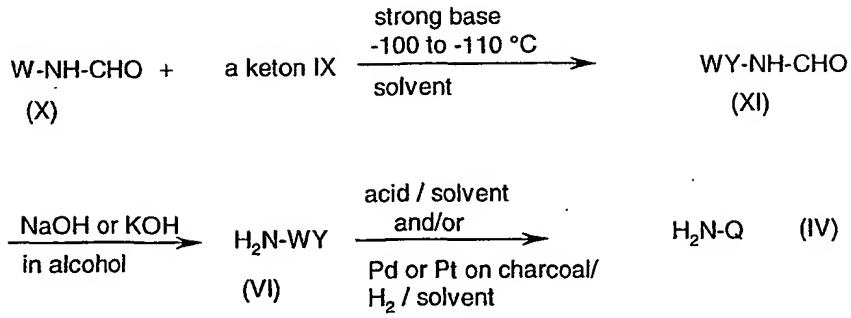
Scheme 2D



The amine intermediates NH_2-Q of formula IV may be prepared according to the following reactions as outlined in Scheme 3.

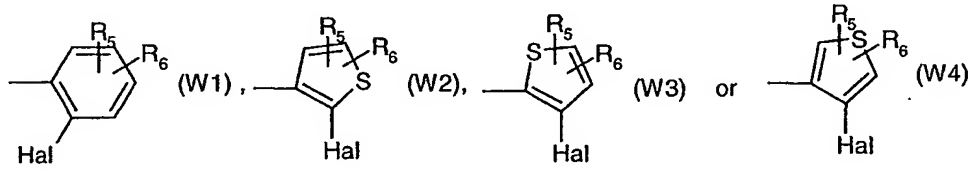
Scheme 3

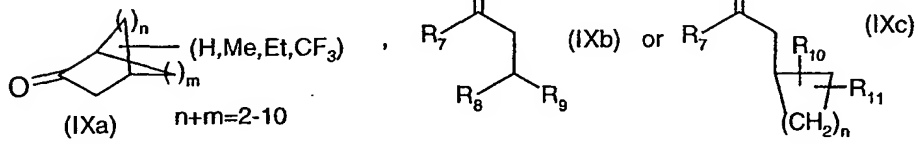
Route a)

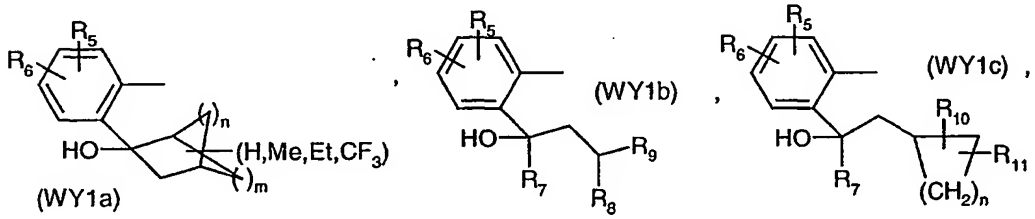


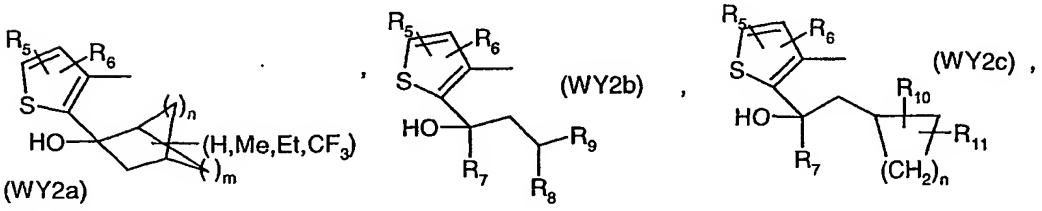
wherein Q, R_5, R_6, R_7, R_8, R_9, R_{10}, R_{11} and n are as described for the compounds of formula I, Hal is Br or I; strong base is n-BuLi, sec.-BuLi, tert.-BuLi, PhLi; and

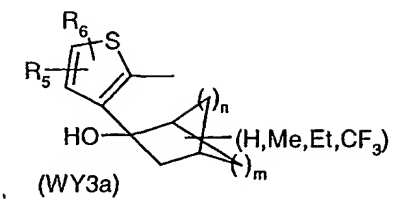
wherein

W is  (W1), (W2), (W3) or (W4)

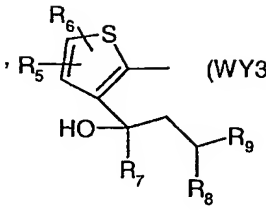
IX is  (IXa) n+m=2-10, (IXb) or (IXc)

WY is  (WY1a), (WY1b), (WY1c)

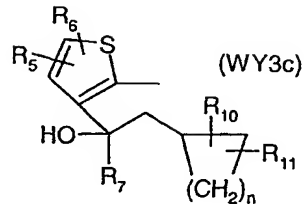




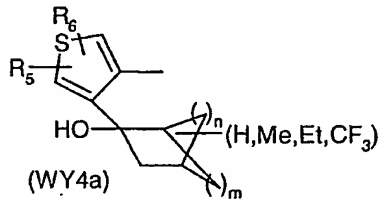
(WY3a)



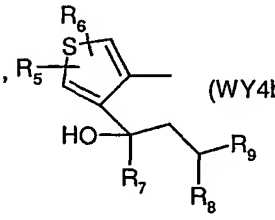
(WY3b),



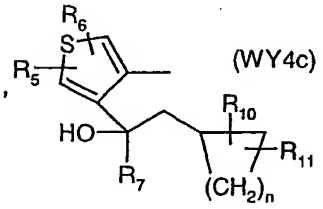
(WY3c),



(WY4a)



(WY4b),

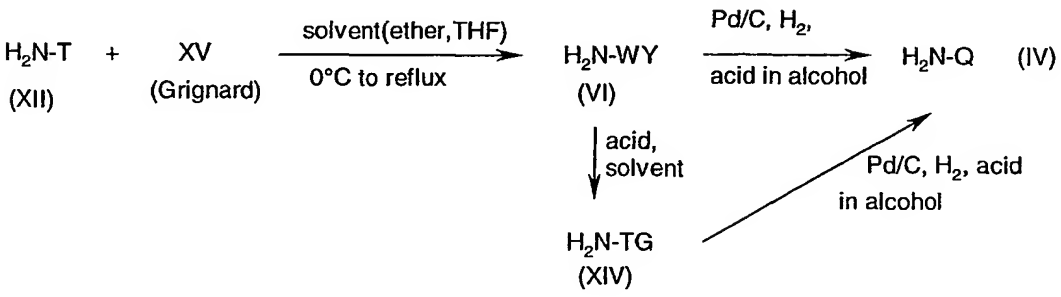


(WY4c),

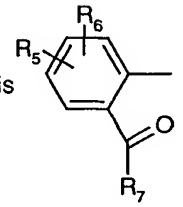
and n+m=2-10

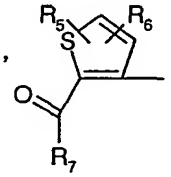
or

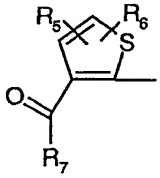
Route b)

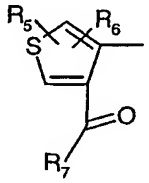


wherein

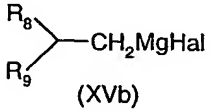
T is 

(T1), 

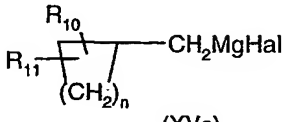
(T2), 

(T3) or 

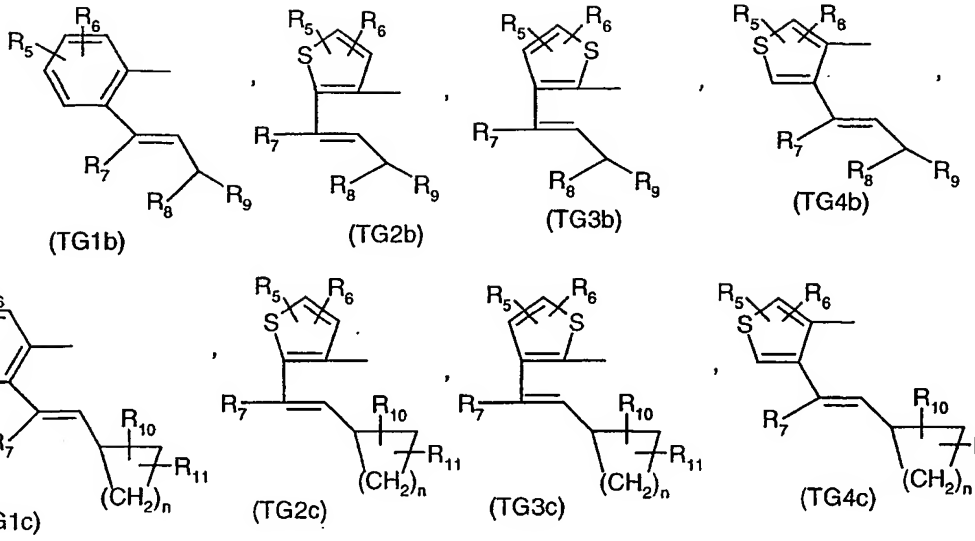
(T4)

XV is 

(XVb)

or 

(XVc)

TG is 

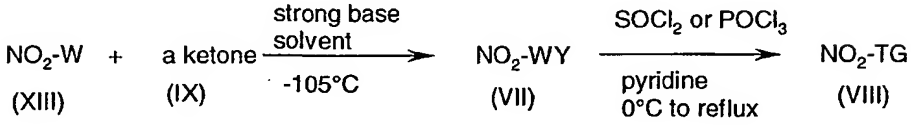
(TG1b) (TG2b) (TG3b) (TG4b)

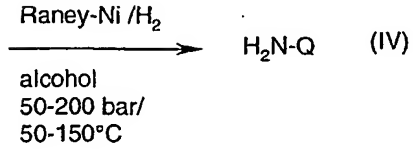
(TG1c) (TG2c) (TG3c) (TG4c)

and wherein isomeric mixtures are possible at the double bond

or

Route c)

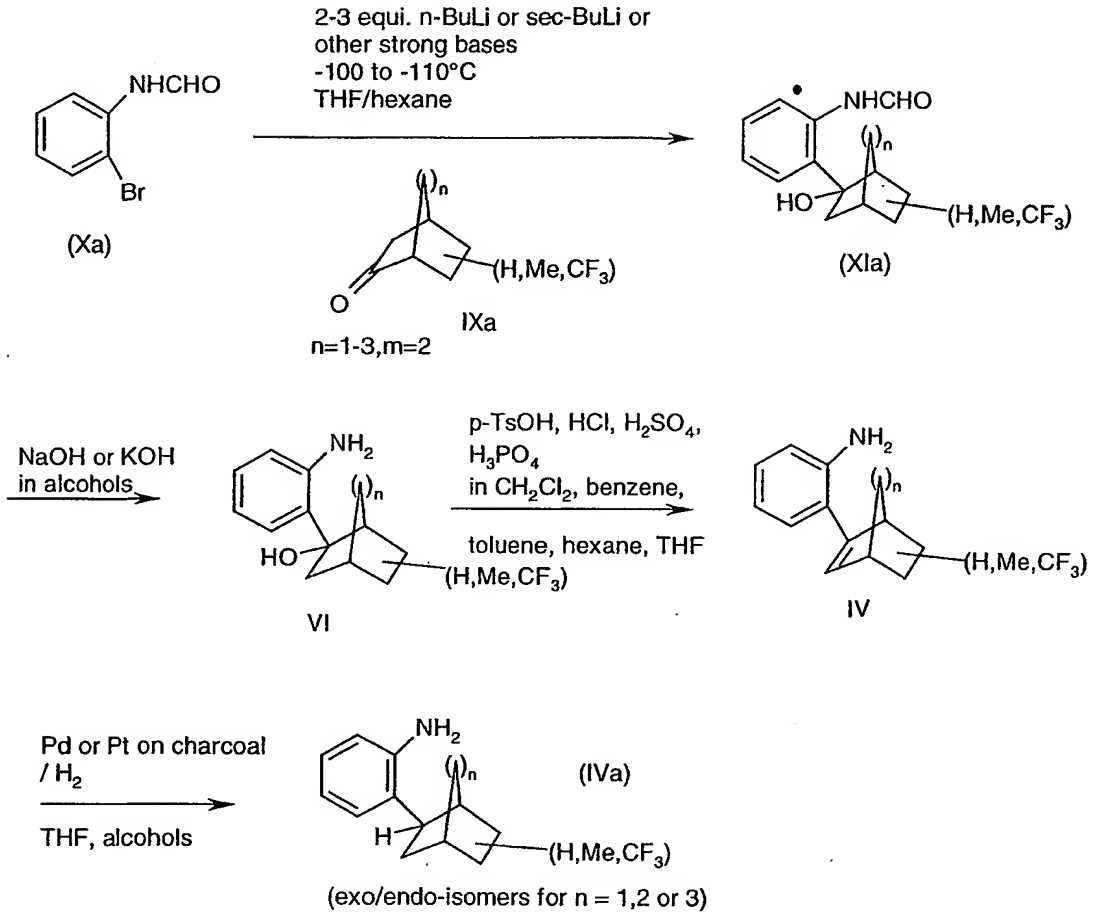




Specific amines of the formula IV can be prepared as follows:

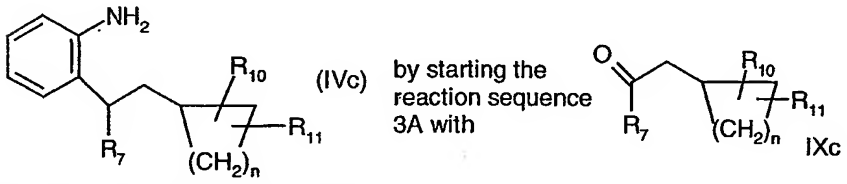
-- The amines H_2N-Q of formula IV, wherein Q = Q1 as defined in formula I and R_4 is bicycloalkyl, bicycloalkenyl or bicycloalkadienyl and R_5 and R_6 are hydrogen may be obtained according to Scheme 3A (Route a).

Scheme 3A

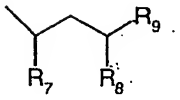


For the synthesis of 2-bicyclo[2.2.1]hept-2-yl phenylamine and other bicyclosystems see for example EP-116044.

According to Scheme 3A the following compounds are also available :

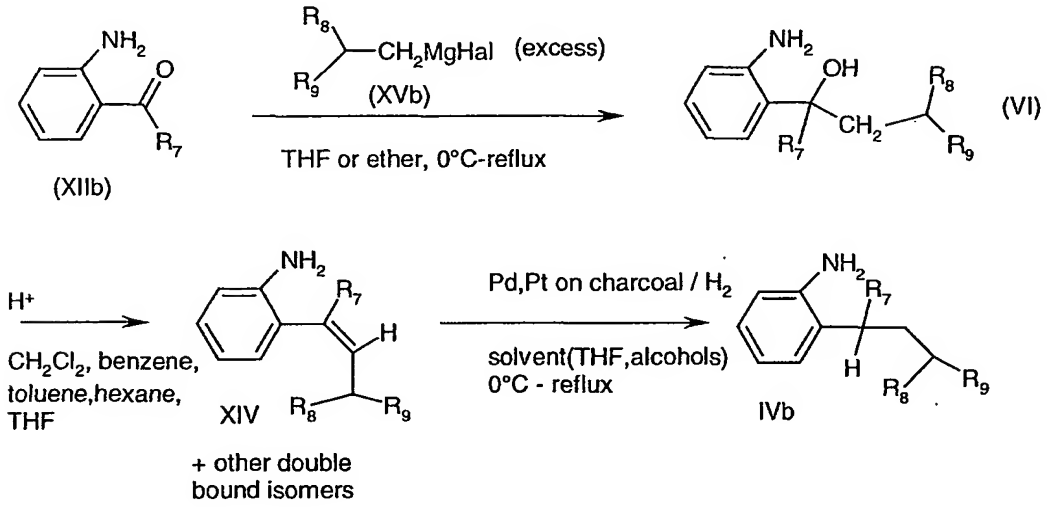


wherein R_5 and R_6 are hydrogen and R_7, R_{10}, R_{11} and n are as defined for formula I.

-- The amines H_2N-Q wherein Q is Q1 and R_4 is a group of the form 

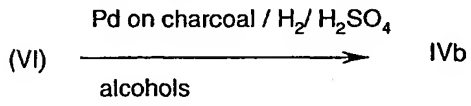
R_5 and R_6 are hydrogen and R_7, R_8 and R_9 are as defined for formula I may be obtained according to Scheme 3B (Route b).

Scheme 3B



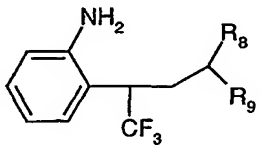
(other syntheses of ortho-alkylsubstituted anilines are also described in EP-824099)

or in a one step hydrogenation of the OH-group of compounds of formula VI

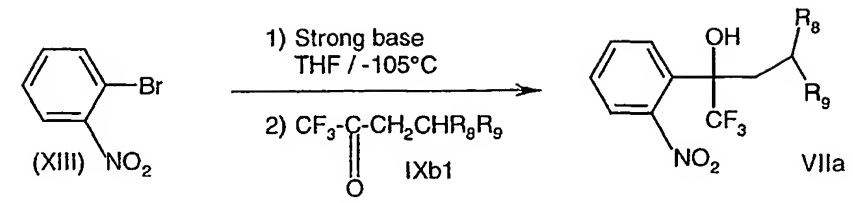


-- Another synthesis of the amine intermediates is outlined in Scheme 3C (Route c).

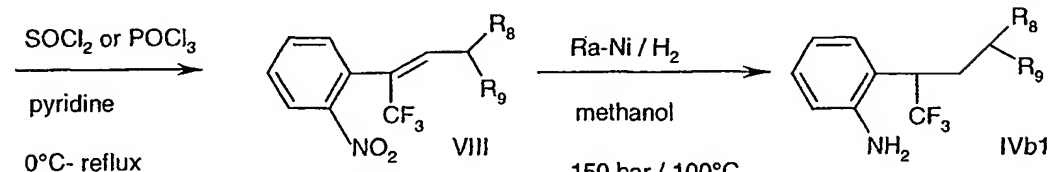
Scheme 3C

for compounds of formula IVb1 

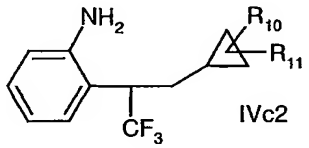
wherein R_7 is CF_3, R_5 and R_6 are hydrogen and R_8 and R_9 are as defined for formula I

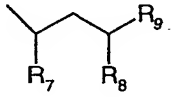


strong base: n-BuLi, sec-BuLi, tert-BuLi, PhLi or others

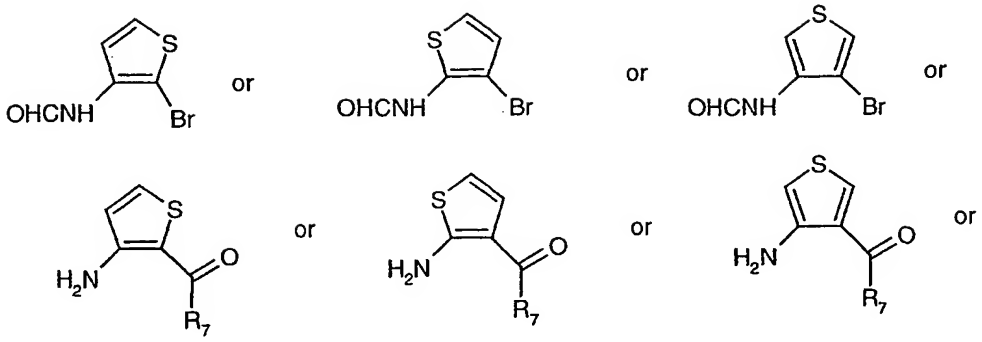


Using the reaction sequence outlined in Scheme 3C the compounds of formula IVc2 wherein R_5 and R_6 are hydrogen, R_7 is CF_3, n=1 and R_{10} and R_{11} are as defined for formula I are also available

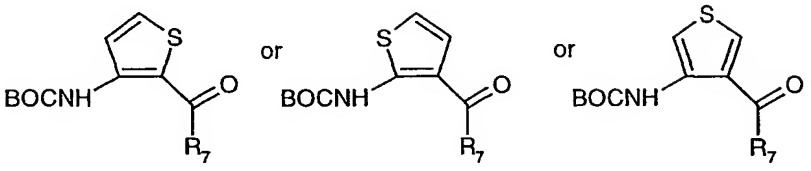


-- The synthesis of the amines IV wherein Q is Q2, Q3 or Q4, R_5 and R_6 are hydrogen and R_4 is bicycloalkyl, bicycloalkenyl, bicycloalkadienyl or a group of the form 

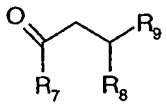
and wherein R_7, R_8 and R_9 are as defined for formula I may be obtained according to scheme 3A) or 3B) starting from the following corresponding thienyl derivatives

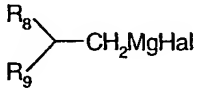


(protected aminothiophenes)



BOC = $-C(O)OC(CH_3)_3$

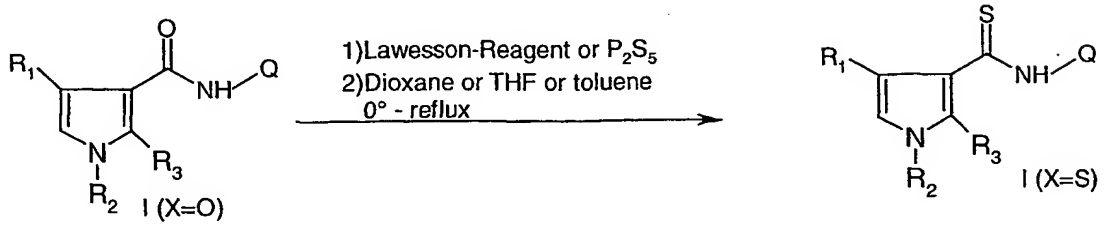
and reacting either with the ketone IXa or IXb  (IXb)

or the Grignard-reagent XVb  (XVb)

The present invention also relates to novel ketones of formula IX.

The carbothioic acid amides of formula I, wherein X=S may be obtained from the compounds of formula I wherein X=O according to Scheme 4.

Scheme 4



I (X=O) I (X=S)

The following phenylamine derivatives of formula IV are new and part of the invention :
2-bicyclo[2.2.2]oct-2-yl-phenylamine;
2-bicyclo[2.2.2]oct-2-en-2-yl-phenylamine;
2-bicyclo[2.2.2]octa-2,5-dien-2-yl-phenylamine;
2-(2-aminophenyl)-1,1,1-trifluoromethyl-4-methyl-pentan-2-ol;
2-(2-aminophenyl)-1-cyclopropyl-propan-2-ol;
2-(2-aminophenyl)-1-cyclopropyl-butan-2-ol;
2-(3-methyl-1-trifluoromethyl-but-1-enyl)-phenylamine;
2-(3-methyl-1-trifluoromethyl-butyl)phenylamine;
2-(2-cyclopropyl-1-methyl-ethyl)phenylamine; and
2-(1-cyclopropylmethyl-propyl)phenylamine.

Surprisingly, it has now been found that the novel compounds of formula I have, for practical purposes, a very advantageous spectrum of activities for protecting plants against diseases that are caused by fungi as well as by bacteria and viruses.
The compounds of formula I can be used in the agricultural sector and related fields of use as active ingredients for controlling plant pests. The novel compounds are distinguished by excellent activity at low rates of application, by being well tolerated by plants and by being environmentally safe. They have very useful curative, preventive and systemic properties and are used for protecting numerous cultivated plants. The compounds of formula I can be used to inhibit or destroy the pests that occur on plants or parts of plants (fruit, blossoms, leaves, stems, tubers, roots) of different crops of useful plants, while at the same time protecting also those parts of the plants that grow later e.g. from phytopathogenic micro-organisms.
It is also possible to use compounds of formula I as dressing agents for the treatment of plant propagation material, in particular of seeds (fruit, tubers, grains) and plant cuttings (e.g. rice), for the protection against fungal infections as well as against phytopathogenic fungi occurring in the soil.

The compounds I are, for example, effective against the phytopathogenic fungi of the following classes: Fungi imperfecti (e.g. Botrytis, Pyricularia, Helminthosporium, Fusarium, Septoria, Cercospora and Alternaria) and Basidiomycetes (e.g. Rhizoctonia, Hemileia, Puccinia). Additionally, they are also effective against the Ascomycetes classes (e.g. Ven-

turia and Erysiphe, Podosphaera, Monilinia, Uncinula) and of the Oomycetes classes (e.g. Phytophthora, Pythium, Plasmopara). Outstanding activity has been observed against powdery mildew (*Erysiphe spp.*). Furthermore, the novel compounds of formula I are effective against phytopathogenic bacteria and viruses (e.g. against Xanthomonas spp, Pseudomonas spp, Erwinia amylovora as well as against the tobacco mosaic virus).

Within the scope of present invention, target crops to be protected typically comprise the following species of plants: cereal (wheat, barley, rye, oat, rice, maize, sorghum and related species); beet (sugar beet and fodder beet); pomes, drupes and soft fruit (apples, pears, plums, peaches, almonds, cherries, strawberries, raspberries and blackberries); leguminous plants (beans, lentils, peas, soybeans); oil plants (rape, mustard, poppy, olives, sunflowers, coconut, castor oil plants, cocoa beans, groundnuts); cucumber plants (pumpkins, cucumbers, melons); fibre plants (cotton, flax, hemp, jute); citrus fruit (oranges, lemons, grapefruit, mandarins); vegetables (spinach, lettuce, asparagus, cabbages, carrots, onions, tomatoes, potatoes, paprika); lauraceae (avocado, cinnamomum, camphor) or plants such as tobacco, nuts, coffee, eggplants, sugar cane, tea, pepper, vines, hops, bananas and natural rubber plants, as well as ornamentals.

The compounds of formula I are used in unmodified form or, preferably, together with the adjuvants conventionally employed in the art of formulation. To this end they are conveniently formulated in known manner to emulsifiable concentrates, coatable pastes, directly sprayable or dilutable solutions, dilute emulsions, wettable powders, soluble powders, dusts, granulates, and also encapsulations e.g. in polymeric substances. As with the type of the compositions, the methods of application, such as spraying, atomizing, dusting, scattering, coating or pouring, are chosen in accordance with the intended objectives and the prevailing circumstances. The compositions may also contain further adjuvants such as stabilizers, antifoams, viscosity regulators, binders or tackifiers as well as fertilizers, micronutrient donors or other formulations for obtaining special effects.

Suitable carriers and adjuvants can be solid or liquid and are substances useful in formulation technology, e.g. natural or regenerated mineral substances, solvents, dispersants, wetting agents, tackifiers, thickeners, binders or fertilizers. Such carriers are for example described in WO 97/33890.

The compounds of formula I are normally used in the form of compositions and can be applied to the crop area or plant to be treated, simultaneously or in succession with further compounds. These further compounds can be e.g. fertilizers or micronutrient donors or other preparations which influence the growth of plants. They can also be selective herbicides as well as insecticides, fungicides, bactericides, nematicides, molluscicides or mixtures of several of these preparations, if desired together with further carriers, surfactants or application promoting adjuvants customarily employed in the art of formulation.
The compounds of formula I can be mixed with other fungicides, resulting in some cases in unexpected synergistic activities.

Mixing components which are particularly preferred are azoles such as azaconazole, bitertanol, propiconazole, difenoconazole, diniconazole, cyproconazole, epoxiconazole, fluquinconazole, flusilazole, flutriafol, hexaconazole, imazalil, imibenconazole, ipconazole, tebuconazole, tetraconazole, fenbuconazole, metconazole, myclobutanil, perfurazoate, penconazole, bromuconazole, pyrifenox, prochloraz, triadimefon, triadimenol, triflumizole or triticonazole; pyrimidinyl carbinoles such as ancymidol, fenarimol or nuarimol; 2-amino-pyrimidine such as bupirimate, dimethirimol or ethirimol; morpholines such as dodemorph, fenpropidin, fenpropimorph, spiroxamin or tridemorph; anilinopyrimidines such as cyprodinil, pyrimethanil or mepanipyrim; pyrroles such as fenpiclonil or fludioxonil; phenylamides such as benalaxyl, furalaxyl, metalaxyl, R-metalaxyl, ofurace or oxadixyl; benzimidazoles such as benomyl, carbendazim, debacarb, fuberidazole or thiabendazole; dicarboximides such as chlozolinate, dichlozoline, iprodine, myclozoline, procymidone or vinclozolin; carboxamides such as carboxin, fenfuram, flutolanil, mepronil, oxycarboxin or thifluzamide; guanidines such as guazatine, dodine or iminoctadine; strobilurines such as azoxystrobin, kresoxim-methyl, metominostrobin, SSF-129, methyl 2-[(2-trifluoromethyl)-pyrid-6-yloxymethyl]-3-methoxyacrylate or 2-[α{[(α-methyl-3-trifluoromethyl-benzyl)imino]-oxy}-o-tolyl]-glyoxylic acid-methylester-O-methyloxime (trifloxystrobin); dithiocarbamates such as ferbam, mancozeb, maneb, metiram, propineb, thiram, zineb or ziram; N-halomethylthio-dicarboximides such as captafol, captan, dichlofluanid, fluoromide, folpet or tolyfluanid; copper compounds such as Bordeaux mixture, copper hydroxide, copper oxychloride, copper sulfate, cuprous oxide, mancopper or oxine-copper; nitrophenol derivatives such as dinocap or nitrothal-isopropyl; organo phosphorous derivatives such as edifenphos, iprobenphos, isoprothiolane, phosdiphen, pyrazophos or toclofos-methyl; and other compounds of diverse structures such as acibenzolar-S-methyl, anilazine, blasticidin-S,

chinomethionat, chloroneb, chlorothalonil, cymoxanil, dichlone, diclomezine, dicloran, diethofencarb, dimethomorph, dithianon, etridiazole, famoxadone, fenamidone, fentin, ferimzone, fluazinam, flusulfamide, fenhexamid, fosetyl-aluminium, hymexazol, kasugamycin, methasulfocarb, pencycuron, phthalide, polyoxins, probenazole, propamocarb, pyroquilon, quinoxyfen, quintozene, sulfur, triazoxide, tricyclazole, triforine, validamycin, (S)-5-methyl-2-methylthio-5-phenyl-3-phenyl-amino-3,5-dihydroimidazol-4-one (RPA 407213), 3,5-dichloro-N-(3-chloro-1-ethyl-1-methyl-2-oxopropyl)-4-methylbenzamide (RH-7281), N-allyl-4,5-dimethyl-2-trimethylsilylthiophene-3-carboxamide (MON 65500), 4-chloro-4-cyano-N,N-dimethyl-5-p-tolylimidazole-1-sulfon-amide (IKF-916), N-(1-cyano-1,2-dimethyl-propyl)-2-(2,4-dichlorophenoxy)-propionamide (AC 382042), or iprovalicarb (SZX 722).

A preferred method of applying a compound of formula I, or an agrochemical composition which contains at least one of said compounds, is foliar application. The frequency of application and the rate of application will depend on the risk of infestation by the corresponding pathogen. However, the compounds of formula I can also penetrate the plant through the roots via the soil (systemic action) by drenching the locus of the plant with a liquid formulation, or by applying the compounds in solid form to the soil, e.g. in granular form (soil application). In crops of water rice such granulates can be applied to the flooded rice field. The compounds of formula I may also be applied to seeds (coating) by impregnating the seeds or tubers either with a liquid formulation of the fungicide or coating them with a solid formulation.

The formulation, i.e. the compositions containing the compound of formula I and, if desired, a solid or liquid adjuvant, are prepared in known manner, typically by intimately mixing and/or grinding the compound with extenders, e.g. solvents, solid carriers and, optionally, surface active compounds (surfactants).

The agrochemical formulations will usually contain from 0.1 to 99 % by weight, preferably from 0.1 to 95 % by weight, of the compound of formula I, 99.9 to 1 % by weight, preferably 99.8 to 5 % by weight, of a solid or liquid adjuvant, and from 0 to 25 % by weight, preferably from 0.1 to 25 % by weight, of a surfactant.

Advantageous rates of application are normally from 5 g to 2 kg of active ingredient (a.i.) per hectare (ha), preferably from 10 g to 1 kg a.i./ha, most preferably from 20 g to 600 g

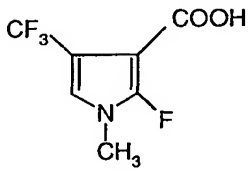
a.i./ha. When used as seed drenching agent, convenient dosages are from 10 mg to 1 g of active substance per kg of seeds.

Whereas it is preferred to formulate commercial products as concentrates, the end user will normally use dilute formulations.

The following non-limiting examples illustrate the above-described invention in more detail. Temperatures are given in degrees Celsius. The following abbreviations are used: m.p.= melting point; b.p.= boiling point. "NMR" means nuclear magnetic resonance spectrum. MS stands for mass spectrum. "%" is percent by weight, unless corresponding concentrations are indicated in other units.

Example 1

2-Fluoro-1-methyl-4-trifluoromethyl-1H-pyrrole-3-carboxylic acid

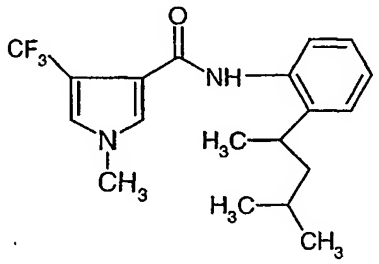


A solution of 1.25g (11mmol) lithiumdiisopropylamide (LDA) à 95% in 20ml absolute THF is dropwise added to a solution of 1.0g (5.2mmol) 1-methyl-4-trifluormethyl-1H-pyrrole-3-carboxylic acid in 60ml THF in such a manner that the temperature remains constant at -75°C. After 3 hours stirring at -75°C, a solution of 1.95g (6.2mmol) N-fluoro-bis(phenylsulfonyl)amine in 20ml absolute THF is added in ca. 30 minutes at a constant temperature of -75°C. Then the cooling is stopped and the reaction mixture is stirred for 16 hours, thereby slowly warming up to room temperature. Then the solvent is removed in a water jet vacuum and the residue is solved in water. After addition of 1N hydrochloric acid (pH ≈ 1) ethylacetate is added and the organic phase extracted twice with additional water. After separation of the organic phase, drying over sodium sulfate and evaporation of the solvent in a water jet vacuum the raw material is obtained. The crude product is purified by column chromatography over silica-gel (eluant : hexane/ethylacetate = 1:1). Yield : 0.65g 2-Fluoro-1-methyl-4-trifluoromethyl-1H-pyrrole-3-carboxylic acid in the form of white crystals; m.p. : 190-191°C.

2-Chloro-1-methyl-4-trifluoromethyl-1H-pyrrole-3-carboxylic acid can be obtained in analogous manner using for example N-chlorsuccinimide as halogenation agent in the reaction described above, m.p. 197-198°C.

Example 2

1-Methyl-4-trifluoromethyl-1H-pyrrole-3-carboxylic acid[2-(1,3-dimethylbutyl)phenyl]amide

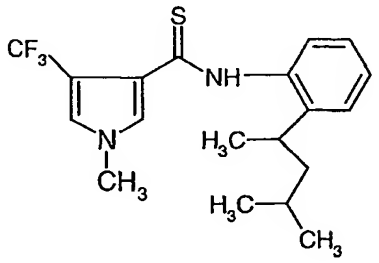


[cmpd. 1.1]

A solution of 0.5g (2.6mmol) 1-methyl-4-trifuoromethylpyrrole-3-carboxylic acid and 0.37g (2.85mmol) oxalylchloride in 20ml methylene chloride is stirred for 3 hours at room temperature in the presence of a catalytic amount of DMF. Then the acid chloride solution is slowly added to a solution of 0.46g (2.6mmol) 2-(1,3-dimethylbutyl)phenylamine, 0.33g (3.4mmol) triethylamine and 15ml methylene chloride. The resulting mixture is then stirred for 16 hours at room temperature. After removal of the solvent in a water jet vacuum, the raw material is taken up in ethylacetate. The ethylacetate phase is washed twice with water and then the organic phase is dried over sodium sulfate. After evaporation of the solvent in a water jet vacuum, the obtained residue is purified by column chromatography over silica-gel (eluant: hexane/ethylacetate = 3:1). Yield: 0.45g 1-Methyl-4-trifluoromethyl-1H-pyrrole-3-carboxylic acid[2-(1,3-dimethylbutyl)phenyl]amide in the form of brownish crystals; m.p. : 83-85°C.

Example 3

1-Methyl-4-trifluoromethyl-1H-pyrrole-3-carbothioic acid[2-(1,3-dimethylbutyl)phenyl]amide

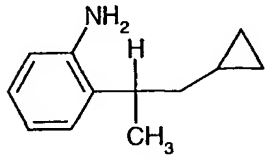


[cmpd. 6.1]

In a sulfonation flask a mixture of 0.6 g 1-Methyl-4-trifluoromethyl-1H-pyrrole-3-carboxylic acid[2-(1,3-dimethylbutyl)phenyl]amide, 0.45 g P_2S_5 and 30 ml dioxane is heated at 70-75°C for 3 hours. After filtration, the solvent is removed in a water jet vacuum and the residue taken up in ethylacetate. The organic phase is washed twice with water and ethylacetate is removed in a water jet vacuum. The crude material is purified by column chromatography over silica gel (eluant: ethylacetate/n-hexane = 1:1). Yield: 0.53 g 1-Methyl-4-trifluoromethyl-1H-pyrrole-3-carbothioic acid[2-(1,3-dimethylbutyl)phenyl]amide in the form of a reddish resin (^{1}H-NMR).

Example 4 (amine intermediate)

2-(2-cyclopropyl-1-methyl-ethyl)phenylamine

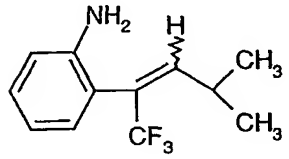


[cmpd. 7.6]

To a solution of 2.96 g (15.5 mmol) of 2-(2-aminophenyl)-1-cyclopropyl-propan-2-ol in 70 ml methanol is added 4.43 g (43.4 mmol) conc. sulfuric acid (96%). The resulting mixture is hydrogenated over 600 mg Pd/C(10%) for 20 hours at 30-35°C. After that time no more hydrogen uptake is detected. The catalyst is filtered off and the solvent removed in a water-jet vacuum. The residue is taken up in ethylacetate/water and the water phase is neutralised by the addition of sodium carbonate. The water phase is extracted twice with ethylacetate, then the combined organic phase is dried over sodium sulfate. After removal of the solvent in a water-jet vacuum, the crude amine is obtained. The obtained raw material is purified by column chromagraphy over silica gel (eluant: hexane/ether = 5:1). Yield: 2.1 g 2-(2-cyclopropyl-1-methyl-ethyl)phenylamine in the form of a brown oil (^{1}H-NMR).

Example 5 (amine intermediate)

2-(3-methyl-1-trifluoromethyl-but-1-enyl)phenylamine, E/Z-isomeric mixture

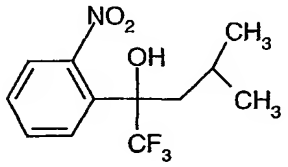


[cmpd. 7.4]

A solution of 1.14 g (4.4 mmol) 1-(3-methyl-1-trifluoromethyl-but-1-enyl)-2-nitrobenzene in 20 ml methanol is hydrogenated over 10% Pd/C (230 mg) at room temperature for 20 minutes. Then the catalyst is filtered off and the solvent removed in a water-jet vacuum. The crude product is purified by column chromatography over silica gel (eluant: methylenechloride/hexane = 2:1). Yield: 0.6 g((sum E + Z isomer) 2-(3-methyl-1-trifluoromethyl-but-1-enyl)phenylamine in the form of a brown oil. After column chromatography both isomers are obtained in pure form (^{1}H-NMR).

Example 6

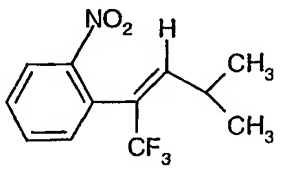
1,1,1-trifluoromethyl-4-methyl-2-(2-nitrophenyl)-pentan-2-ol



To a solution of 20.2 g (0.1 mol) 2-bromonitrobenzene in 300 ml abs. tetrahydrofurane is added 81 ml of sec. BuLi (0.105 mol) over a period of 30 minutes in such a manner that the internal temperature remains constant at –103 to –107°C. After stirring for 70 minutes at –103 to –107°C a solution of 20.0 g (0.13 mol) of trifluoromethylisobutylketone in 150 ml abs. tetrahydrofurane is added over a period of 20 minutes in such a manner that the temperature remains constant at –105°C (± 2°C). After stirring for 4 hours at –105°C the temperature is raised to –20°C and a solution of 150 ml of saturated ammoniumchloride solution is added. Then 1 l of ethylacetate is added and the organic phase is washed 3 times with water. After drying the organic phase over sodium sulfate and distilling off the solvent in a water-jet vacuum the raw-material is obtained. Purification is achieved by column chromatography over silica gel (eluant: hexane/ethylacetate = 5:1). Yield: 8.2 g 1,1,1-trifluoromethyl-4-methyl-2-(2-nitrophenyl)pentan-2-ol in the form of a brownish powder; m.p.: 103-105°C.

Example 7

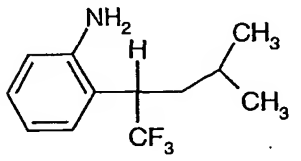
1-(3-methyl-1-trifluoromethyl-but-1-enyl)-2-nitrobenzene (E/Z-mixture)



To a solution of 10.8 g (39 mmol) 1,1,1-trifluoromethyl-4-methyl-2-(2-nitrophenyl)pentan-2-ol in 110 ml of abs. pyridine is added slowly 13.9 g (117 mmol) thionylchloride at a temperature of 0-5°C. Then the mixture is heated at 90-95°C for 1 hour. After cooling the reaction mixture is added to ice water. The resulting solution is extracted carefully with ethylacetate and after drying of the organic phase over sodium sulfate and distilling off the solvent in a water-jet vacuum, the crude product is obtained. Purification is achieved by column chromatography over silica gel (eluant: methylene chloride/hexane = 1:1). Yield: 5.2 g 1-(3-methyl-1-trifluoromethyl-but-1-enyl)-2-nitrobenzene in the form of a brownish oil (^{1}H-NMR).

Example 8 (amine intermediate)

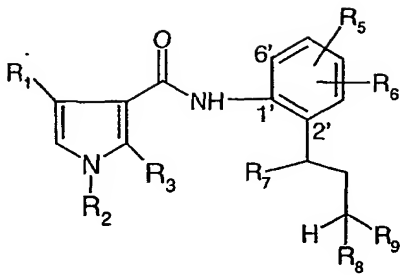
2-(3-methyl-1-trifluoromethyl-butyl)phenylamine



[cmpd. 7.5]

A solution of 2.98 g (12.9 mmol) 1-(3-methyl-1-trifluoromethyl-but-1-enyl)-2-nitrobenzene in 30 ml methanol is hydrogenated over Raney-Nickel (ethanol) at 100°C and 150 bar for 10 hours. Then the catalyst is filtered off and the solvent removed in a water-jet vacuum. The obtained crude product is purified by column chromatography over silica gel (eluant: hexane/methylene chloride = 1:2). Yield: 1.9 g 2-(3-methyl-1-trifluoromethyl-butyl)phenylamine in the form of a brown oil (^{1}H-NMR).

Table 1



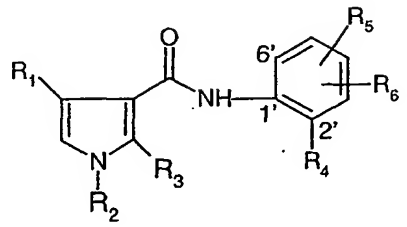
Ia

(md = mixture of diastereoisomers)

Cmpd. no.	R_1	R_2	R_3	R_5	R_6	R_7	R_8	R_9	phys. data m.p.°C
1.1	CF_3	Me	H	H	H	Me	Me	Me	83-85
1.2	CF_3	CH_2OMe	H	H	H	Me	Me	Me	75-77
1.3	CF_3	Me	H	H	H	CF_3	Me	Me	98-100
1.4	CF_3	Me	H	H	H	Me	CF_3	CF_3	
1.5	CF_3	Me	H	H	H	Me	Me	Et	93-97 (md)
1.6	CF_3	CH_2OMe	H	H	H	Me	Me	Et	
1.7	CF_3	Me	H	6'-F	H	Me	Me	Me	
1.8	CF_3	Me	H	5'-F	H	Me	Me	Me	
1.9	CF_3	Me	H	H	H	Me	Et	Et	84-86
1.10	CF_3	Me	F	H	H	Me	Me	Me	
1.11	CF_3	CH_2OMe	F	H	H	Me	Me	Me	
1.12	CF_3	Me	F	H	H	Me	Me	Et	resin; ^{1}H-NMR, MS
1.13	CF_3	Me	F	H	H	CF_3	Me	Me	resin; ^{1}H-NMR, MS
1.14	CF_3	Me	F	H	H	CF_3	Me	Et	
1.15	CF_2H	Me	H	H	H	Me	Me	Me	
1.16	CF_2H	Me	H	H	H	Me	Me	Et	
1.17	CF_2H	Me	H	H	H	CF_3	Me	Me	Resin
1.18	CF_2H	Me	H	H	H	Me	CF_3	CF_3	
1.19	CF_2H	Me	H	H	H	CF_2H	Me	Me	
1.20	CF_2H	CH_2OMe	H	H	H	Me	Me	Me	

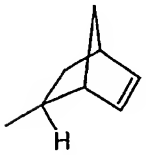
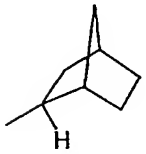
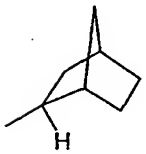
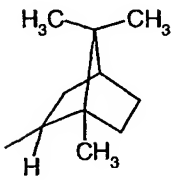
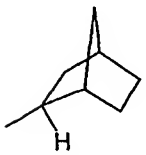
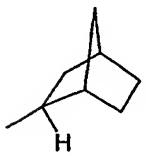
1.21	CF_2H	CH_2OMe	H	H	H	Me	Me	Et	
1.22	CF_2H	Me	F	H	H	Me	Me	Me	
1.23	CF_2H	Me	F	H	H	Me	Me	Et	
1.24	CFH_2	Me	H	H	H	Me	Me	Me	
1.25	CFH_2	Me	H	H	H	Me	Me	Et	
1.26	CFH_2	Me	F	H	H	Me	Me	Me	
1.27	CFH_2	Me	F	H	H	Me	Me	Et	
1.28	CF_3	Me	H	H	H	Et	Me	Me	Resin; ^{1}H-NMR, $M^+ = 366$
1.29	CF_3	Me	H	H	H	Et	Me	Et	oil; $M^+ = 380$
1.30	CF_3	Me	F	H	H	Et	Me	Me	
1.31	CF_3	Me	F	H	H	Et	Me	Et	
1.32	CF_2H	Me	H	H	H	Et	Me	Me	
1.33	CF_2H	Me	H	H	H	Et	Me	Et	
1.34	CF_2H	Me	F	H	H	Et	Me	Me	
1.35	CFH_2	Me	H	H	H	Et	Me	Me	

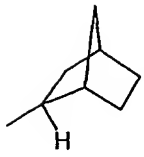
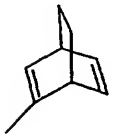
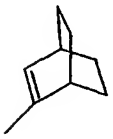
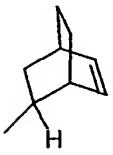
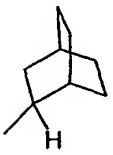
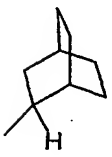
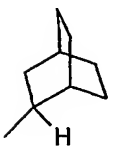
Table 2

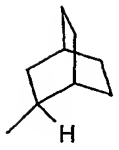
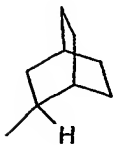
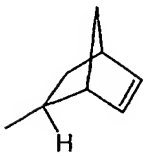
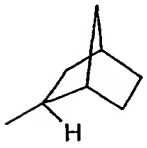
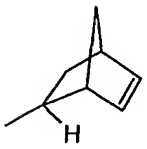
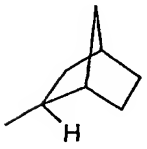
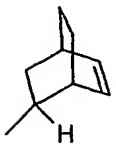


Ib

Cmpd. no.	R_1	R_2	R_3	R_4	R_5	R_6	Phys.data m.p.°C
2.1	CF_3	Me	H		H	H	

2.2	CF_3	Me	H		H	H	Resin (^{1}H-NMR, MS)
2.3	CF_3	Me	H		H	H	
2.4	CF_3	Me	H		H	H	136-137
2.5	CF_3	Me	H		6'-F	H	
2.6	CF_3	Me	H		H	H	
2.7	CF_3	CH_2OMe	H		H	H	
2.8	CF_2H	Me	H		H	H	

2.9	CF_2H	Me	H		H	H	
2.10	CF_3	Me	H		H	H	105-107
2.11	CF_3	Me	H		H	H	110-112
2.12	CF_3	Me	H		H	H	
2.13	CF_3	Me	H		H	H	127-129
2.14	CF_3	CH_2OMe	H		H	H	
2.15	CF_3	Me	H		4'-F	H	

2.16	CF_3	CH_2OMe	H		4'-F	H
2.17	CF_2H	Me	H		H	H
2.18	CF_3	Me	F		H	H
2.19	CF_3	Me	F		H	H
2.20	CF_3	CH_2OMe	F		H	H
2.21	CF_3	CH_2OMe	F		H	H
2.22	CF_3	Me	F		H	H

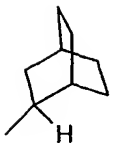
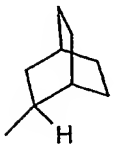
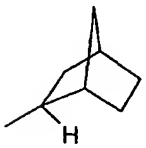
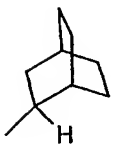
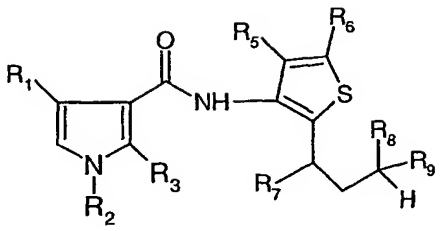
2.23	CF_3	Me	F		H	H	176-178
2.24	CF_3	CH_2OMe	F		H	H	
2.25	CF_3	Me	Me		H	H	
2.26	CF_3	Me	Me		H	H	

Table 3

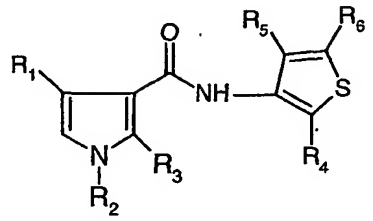


Ic

Cmpd. no.	R_1	R_2	R_3	R_5	R_6	R_7	R_8	R_9	Phys. data m.p.°C
3.1	CF_3	Me	H	H	H	Me	Me	Me	92-93
3.2	CF_3	CH_2OMe	H	H	H	Me	Me	Me	
3.3	CF_3	Me	H	H	H	CF_3	Me	Me	
3.4	CF_3	Me	H	H	H	Me	CF_3	CF_3	
3.5	CF_3	Me	H	H	H	Me	Me	Et	

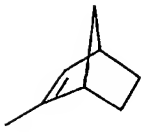
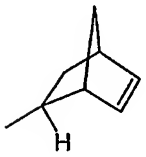
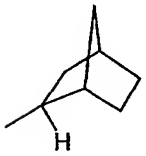
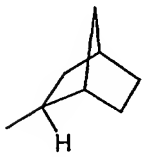
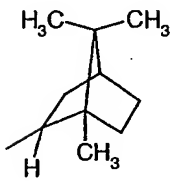
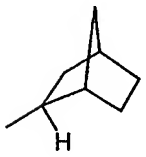
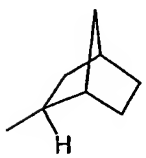
3.6	CF_3	CH_2OMe	H	H	H	Me	Me	Et	
3.7	CF_3	Me	H	6'-F	H	Me	Me	Me	
3.8	CF_3	Me	H	5'-F	H	Me	Me	Me	
3.9	CF_3	Me	H	H	H	Me	Et	Et	
3.10	CF_3	Me	F	H	H	Me	Me	Me	Oil
3.11	CF_3	CH_2OMe	F	H	H	Me	Me	Me	
3.12	CF_3	Me	F	H	H	Me	Me	Et	
3.13	CF_3	Me	F	H	H	CF_3	Me	Me	
3.14	CF_3	Me	F	H	H	CF_3	Me	Et	
3.15	CF_2H	Me	H	H	H	Me	Me	Me	Oil
3.16	CF_2H	Me	H	H	H	Me	Me	Et	
3.17	CF_2H	Me	H	H	H	CF_3	Me	Me	
3.18	CF_2H	Me	H	H	H	Me	Me	Me	
3.19	CFH_2	Me	H	H	H	Me	Me	Me	
3.20	CFH_2	Me	H	H	H	Me	Me	Et	
3.21	CFH_2	Me	H	H	H	CF_3	Me	Me	
3.22	CFH_2	Me	H	H	H	Me	Me	Me	

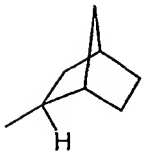
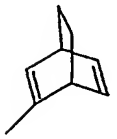
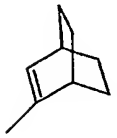
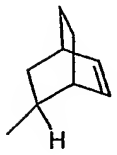
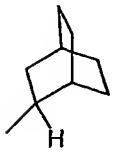
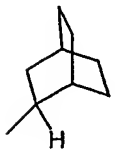
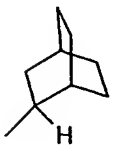
Table 4

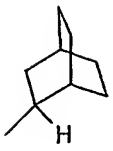
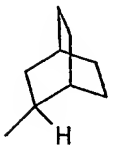
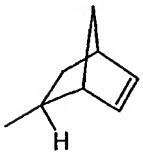
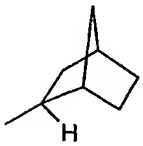
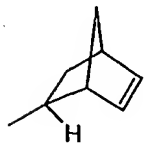
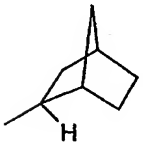
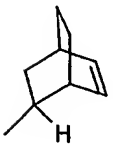


Id

Cmpd. no.	R_1	R_2	R_3	R_4	R_5	R_6	phys.data m.p.°C
4.1	CF_3	Me	H		H	H	

4.2	CF_3	Me	H		H	H	Resin
4.3	CF_3	Me	H		H	H	
4.4	CF_3	Me	H		H	H	Resin
4.5	CF_3	Me	H		6'-F	H	
4.6	CF_3	Me	H		H	H	
4.7	CF_3	CH_2OMe	H		H	H	
4.8	CF_2H	Me	H		H	H	

4.9	CF_2H	Me	H		H	H
4.10	CF_3	Me	H		H	H
4.11	CF_3	Me	H		H	H
4.12	CF_3	Me	H		H	H
4.13	CF_3	Me	H		H	H
4.14	CF_3	CH_2OMe	H		H	H
4.15	CF_3	Me	H		4'-F	H

4.16	CF_3	CH_2OMe	H		4'-F	H
4.17	CF_2H	Me	H		H	H
4.18	CF_3	Me	F		H	H
4.19	CF_3	Me	F		H	H
4.20	CF_3	CH_2OMe	F		H	H
4.21	CF_3	CH_2OMe	F		H	H
4.22	CF_3	Me	F		H	H

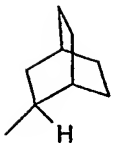
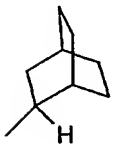
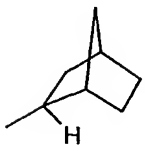
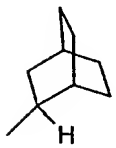
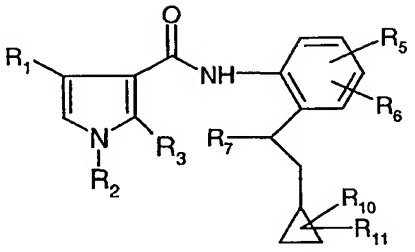
4.23	CF_3	Me	F		H	H
4.24	CF_3	CH_2OMe	F		H	H
4.25	CF_3	Me	Me		H	H
4.26	CF_3	Me	Me		H	H

Table 5

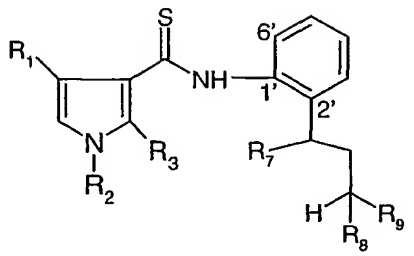


Id

Cmpd. no.	R_1	R_2	R_3	R_5	R_6	R_7	R_{10}	R_{11}	phys.data m.p.°C
5.1	CF_3	Me	H	H	H	Me	H	H	109-110
5.2	CF_3	CH_2OMe	H	H	H	Me	H	H	
5.3	CF_3	Me	H	H	H	CF_3	H	H	
5.4	CF_3	Me	H	H	H	Me	Cl	Cl	
5.5	CF_3	CH_2OMe	H	H	H	CF_3	H	H	

5.6	CF_3	Me	F	H	H	Me	H	H	
5.7	CF_3	CH_2OMe	F	H	H	Me	H	H	
5.8	CF_3	Me	F	H	H	CF_3	H	H	
5.9	CF_3	CH_2OMe	F	H	H	Me	H	H	
5.10	CF_3	CH_2OMe	F	H	H	CF_3	H	H	
5.11	CF_3	Me	F	H	H	Me	Cl	Cl	
5.12	CF_2H	Me	H	H	H	Me	H	H	
5.13	CF_2H	Me	H	H	H	CF_3	H	H	
5.14	CF_2H	CH_2OMe	H	H	H	Me	H	H	
5.15	CF_2H	CH_2OMe	H	H	H	CF_3	H	H	
5.16	CF_2H	Me	F	H	H	Me	H	H	
5.17	CF_2H	Me	F	H	H	CF_3	H	H	
5.18	CF_2H	CH_2OMe	F	H	H	Me	H	H	
5.19	CF_2H	CH_2OMe	F	H	H	CF_3	H	H	
5.20	CF_2H	Me	H	H	H	Me	Cl	Cl	
5.21	CF_2H	CH_2OMe	H	H	H	Me	Cl	Cl	
5.22	CFH_2	Me	H	H	H	Me	H	H	
5.23	CFH_2	Me	H	H	H	Et	H	H	
5.24	CF_2H	Me	F	H	H	Me	H	H	
5.25	CF_3	Me	H	H	H	Et	H	H	59-61
5.26	CF_3	Me	F	H	H	Et	H	H	
5.27	CF_2H	Me	H	H	H	Et	H	H	
5.28	CF_2H	Me	F	H	H	Et	H	H	

Table 6

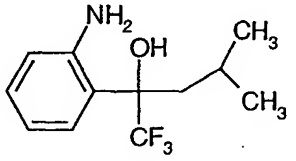
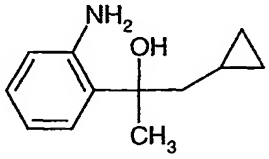
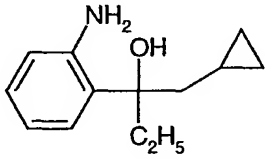
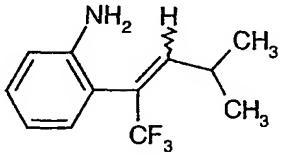
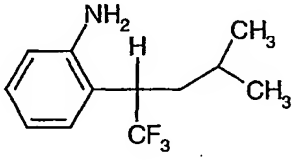
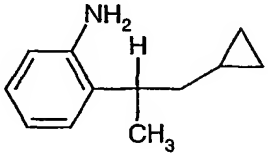
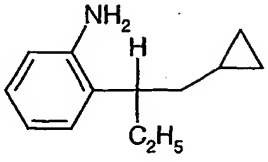


Ie

(md = mixture of diastereoisomers)

Cmpd. no.	R_1	R_2	R_3	R_7	R_8	R_9	Phys. Data m.p.°C
6.1	CF_3	Me	H	Me	Me	Me	resin;^{1}H-NMR;M^+=368
6.2	CF_3	CH_2OMe	H	Me	Me	Me	
6.3	CF_3	Me	H	CF_3	Me	Me	
6.4	CF_3	Me	H	Me	CF_3	CF_3	
6.5	CF_3	Me	H	Me	Me	Et	md;resin;^{1}H-NMR;M^+=382
6.6	CF_3	CH_2OMe	H	Me	Me	Et	
6.7	CF_3	Me	H	Me	Et	Et	
6.8	CF_3	Me	F	Me	Me	Me	Resin; M^+ = 386
6.9	CF_3	CH_2OMe	F	Me	Me	Me	
6.10	CF_3	Me	F	Me	Me	Et	
6.11	CF_3	Me	F	CF_3	Me	Me	
6.12	CF_3	Me	F	CF_3	Me	Et	
6.13	CF_2H	Me	H	Me	Me	Me	
6.14	CF_2H	Me	H	Me	Me	Et	
6.15	CF_2H	Me	H	CF_3	Me	Me	
6.16	CF_2H	Me	H	Me	Me	Me	

Table 7: Amine-Intermediates

Cmpd.No.		Phys.data (m.p.°C or NMR)
7.1		84-86
7.2		Oil; ^{1}H-NMR
7.3		Oil; ^{1}H-NMR
7.4 7.4.1: E-isomer 7.4.2: Z-isomer	 E/Z-mixture	Oil; ^{1}H-NMR
7.5		Oil; ^{1}H-NMR
7.6		Oil; ^{1}H-NMR
7.7		Oil; ^{1}H-NMR

^{1}H-NMR Table

Compd. No.	^{1}H-NMR-data (ppm/multiplicity/number of protons; solvent $CDCl_3$)
6.1	0.82/2xd/6H; 1.19/d/3H; 1.35-1.60/m/1H; 3.70/s/3H; 6.99/d/1H; 7.2-7.4/m/4H; 7.61/d/1H; 8.70/s(broad)/1H
6.5	0.75-0.88/m/12H; 1.0-1.65/m/6H; 1.18/d/3H; 1.20/d/3H; 3.0/m/2H; 3.70/s/6H; 7.0/d/2H; 7.2-7.4/m/8H; 7.61/d/2H; 8.7/s/2H
7.2	0.1/m/2H; 0.45/m/2H; 0.65/m/1H; 1.69/s/3H; 1.80/m/1H; 2.0/m/1H; 3.7/s(broad)/3H(OH+NH_2); 6.60-6.70/m/2H; 6.98-7.11/m/2H
7.3	0.01/m/2H; 0.35/m/2H; 0.55/m/2H; 0.75/t/3H; 1.51/m/1H; 1.8-2.05/m/3H; 3.72/s(broad)/3H(OH+NH_2); 6.47-6.59/m/2H; 6.91/m/2H
7.4.1 (E-isomer)	1.09/d/6H; 3.02/m/1H; 3.60/s(broad)/2H(NH_2); 5.81/d/1H; 6.72/m/2H; 6.99/dxd/1H; 7.15/txd/1H
7.4.2 (Z-isomer)	0.91/d/3H; 1.03/d/3H; 2.25/m/1H; 3.58/s(broad)/2H; 6.36/dxd/1H; 6.78/m/2H; 6.99/dxd/1H; 7.18/txd/1H
7.5	0.83/d/3H; 0.87/d/3H; 1.40/m/1H; 1.69/m/1H; 1.99/m/1H; 3.6/m/3H(NH_2+H-benzylic); 6.75/dxd/1H; 6.85/t/1H; 7.09-7.2/m/2H
7.6	0.05/m/2H; 0.4/m/2H; 0.69/m/1H; 1.29/d/3H; 1.35/m/1H; 1.60/m/1H; 2.88/m/1H; 3.65/s(broad)/2H(NH_2); 6.68/d/1H; 6.85/t/1H; 7.0/txd/1H; 7.1/dxd/1H
7.7	0.01/m/2H; 0.38/m/2H; 0.60/m/1H; 0.82/t/3H; 1.32/m/1H; 1.52-1.80/m/3H; 2.68/m/1H; 3.65/s(broad)/2H(NH_2); 6.69/d/1H; 6.78/t/1H; 7.0/txd/1H; 7.08/dxd/1H
1.28	0.78-0.85/t+d/9H; 1.35-1.69/m/5H; 2.85/m/1H; 3.70/s/3H; 7.0/d/1H; 7.20/m/3H; 7.37/d/1H; 7.58/s(broad)/1H; 7.7/m/1H

Formulation Examples for compounds of formula I

Working procedures for preparing formulations of the compounds of formula I such as Emulsifiable concentrates, Solutions, Granulates, Dusts and Wettable powders are described in WO 97/33890.

Biological Examples: Fungicidal actions

Example B-1: Action against *Puccinia recondita* / wheat (Brownrust on wheat)

1 week old wheat plants cv. Arina are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. One day after application wheat plants are inoculated by spraying a spore suspension (1 x 10^5 uredospores/ml) on the test plants. After an incubation period of 2 days at 20° C and 95% r. h. plants are kept in a greenhouse for 8 days at 20° C and 60% r.h. The disease incidence is assessed 10 days after inoculation.

Compounds of Tables 1 to 6 show good activity in these tests (< 20% infestation).

Example B-2: Action against *Podosphaera leucotricha* / apple (Powdery mildew on apple)

5 week old apple seedlings cv. McIntosh are treated with the formulated test compound (0.002% active ingredient) in a spray chamber. One day after application apple plants are inoculated by shaking plants infected with apple powdery mildew above the test plants. After an incubation period of 12 days at 22° C and 60% r. h. under a light regime of 14/10 h (light/dark) the disease incidence is assessed.

Compounds of Tables 1 to 6 show good activity in this test.

Example B-3: Action against *Venturia inaequalis* / apple (Scab on apple)

4 week old apple seedlings cv. McIntosh are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. One day after application apple plants are inoculated by spraying a spore suspension (4 x 10^5 conidia/ml) on the test plants. After an incubation period of 4 days at 21° C and 95% r. h. the plants are placed for 4 days at 21° C and 60% r. h. in a greenhouse. After another 4 day incubation period at 21° C and 95% r. h. the disease incidence is assessed.

Compounds of Tables 1 to 6 show good activity in this test.

Example B-4: Action against *Erysiphe graminis* / barley (Powdery mildew on barley)

1 week old barley plants cv. Express are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. One day after application barley plants are inoculated by shaking powdery mildew infected plants above the test plants. After an incubation period of 6 days at 20° C / 18°C (day/night) and 60% r. h. in a greenhouse the disease incidence is assessed.

Compounds of Tables 1 to 6 show good activity in this test.

Example B-5: Action against *Botrytis cinerea* / apple (Botrytis on apple fruits)

In an apple fruit cv. Golden Delicious 3 holes are drilled and each filled with 30 µl droplets of the formulated test compound (0.002% active ingredient). Two hours after application 50 µl of a spore suspension of *B. cinerea* (4 x 10^5 conidia/ml) are pipetted on the application sites. After an incubation period of 7 days at 22° C in a growth chamber the disease incidence is assessed.

Compounds of Tables 1 to 6 show good activity in this test.

Example B-6: Action against *Botrytis cinerea* / grape (Botrytis on grapes)

5 week old grape seedlings cv. Gutedel are treated with the formulated test compound (0.002% active ingredient) in a spray chamber. Two days after application grape plants are inoculated by spraying a spore suspension (1 x 10^6 conidia/ml) on the test plants. After an incubation period of 4 days at 21° C and 95% r. h. in a greenhouse the disease incidence is assessed.

Compounds of Tables 1 to 6 show good activity in this test.

Example B-7: Action against *Botrytis cinerea* / tomato (Botrytis on tomatoes)

4 week old tomato plants cv. Roter Gnom are treated with the formulated test compound (0.002% active ingredient) in a spray chamber. Two days after application tomato plants are inoculated by spraying a spore suspension (1 x 10^5 conidia/ml) on the test plants. After an incubation period of 4 days at 20° C and 95% r. h. in a growth chamber the disease incidence is assessed.

Compounds of Tables 1 to 6 show good activity in this test.

Example B-8: Action against *Pyrenophora teres* / barley (Net blotch on barley)

1 week old barley plants cv. Express are treated with the formulated test compound (0.002% active ingredient) in a spray chamber. Two days after application barley plants are inoculated by spraying a spore suspension (3 x 10^4 conidia/ml) on the test plants. After an incubation period of 2 days at 20° C and 95% r. h. plants are kept for 2 days at 20° C and 60% r.h. in a greenhouse. The disease incidence is assessed 4 days after inoculation.

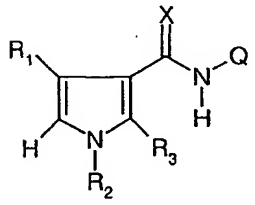
Compounds of Tables 1 to 6 show good activity in this test.

Example B-9: Action against *Septoria nodorum* / wheat (Septoria leaf spot on wheat)

1 week old wheat plants cv. Arina are treated with the formulated test compound (0.02% active ingredient) in a spray chamber. One day after application wheat plants are inoculated by spraying a spore suspension (5×10^5 conidia/ml) on the test plants. After an incubation period of 1 day at 20° C and 95% r. h. plants are kept for 10 days at 20° C and 60% r.h. in a greenhouse. The disease incidence is assessed 11 days after inoculation. Compounds of Tables 1 to 6 show good activity in this test.

What is claimed is

1. A pyrrolecarboxylic acid amide or pyrrolecarbothioic acid amide of the formula I



I

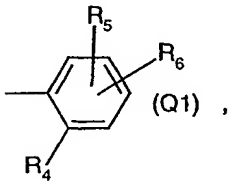
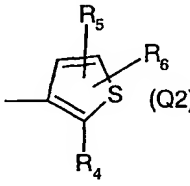
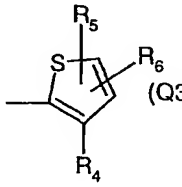
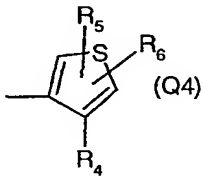
wherein

X is oxygen or sulfur;

R_1 is CF_3, CF_2H or CFH_2;

R_2 is C_1-C_3alkyl, C_1-C_3haloalkyl, C_1-C_3alkoxy-C_1-C_3alkyl or C_1-C_3haloalkoxy-C_1-C_3alkyl;

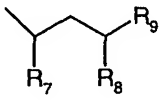
R_3 is hydrogen, methyl, CF_3 or fluoro;

Q is  (Q1) ,  (Q2) ,  (Q3) ,  (Q4) ;

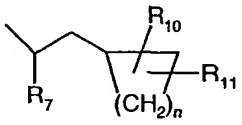
R_4 is C_6-C_{14}bicycloalkyl unsubstituted or substituted by methyl, ethyl or CF_3;

C_6-C_{14}bicycloalkenyl unsubstituted or substituted by methyl, ethyl or CF_3;

C_6-C_{14}bicycloalkadienyl unsubstituted or substituted by methyl, ethyl or CF_3; a group of the form

 wherein R_7, R_8 and R_9 are independently of each other C_1-C_3alkyl or

C_1-C_3haloalkyl; or a group

 wherein R_{10} and R_{11} are independently of each other hydrogen or

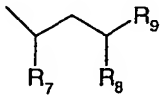
halogen and n = 1 or 2; and

R_5 and R_6 are independently of each other hydrogen or halogen.

2. A compound of formula I according to claim 1, wherein
X is oxygen.

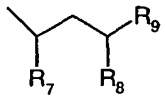
3. A compound of formula I according to claim 1, wherein
X is sulfur.

4. A compound of formula I according to claim 1, wherein
R_1 is CF_3;
R_2 is C_1-C_3alkyl, C_1-C_3haloalkyl or C_1-C_3alkoxy-C_1-C_3alkyl ;
R_3 is hydrogen or fluoro;
Q is Q1;
R_4 is C_6-C_{10}bicycloalkyl unsubstituted or substituted by methyl, ethyl or CF_3;
C_6-C_{10}bicycloalkenyl unsubstituted or substituted by methyl, ethyl or CF_3;
C_6-C_{10}bicycloalkadienyl unsubstituted or substituted by methyl, ethyl or CF_3; a group of the form



wherein R_7, R_8 and R_9 are independently of each other C_1-C_3alkyl or
C_1-C_3haloalkyl; and
R_5 and R_6 are independently of each other hydrogen, chloro or fluoro.

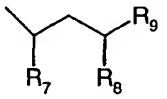
5. A compound of formula I according to claim 4, wherein
R_4 is a group of the form



wherein R_7, R_8 and R_9 are independently of each other C_1-C_3alkyl or
C_1-C_3haloalkyl.

6. A compound of formula I according to claim 1, wherein
R_1 is CF_3;
R_2 is C_1-C_3alkyl, C_1-C_3haloalkyl or C_1-C_3alkoxy-C_1-C_3alkyl;
R_3 is hydrogen or fluoro;
Q is Q2, Q3 or Q4;

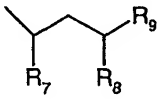
R_4 is C_6-C_{10}bicycloalkyl unsubstituted or substituted by methyl, ethyl or CF_3;
C_6-C_{10}bicycloalkenyl unsubstituted or substituted by methyl, ethyl or CF_3;
C_6-C_{10}bicycloalkadienyl unsubstituted or substituted by methyl, ethyl or CF_3; a group of the form



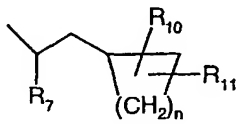
wherein R_7, R_8 and R_9 are independently of each other C_1-C_3alkyl or
C_1-C_3haloalkyl; and
R_5 and R_6 are independently of each other hydrogen, chloro or fluoro.

7. A compound of formula I according to claim 6, wherein
Q is Q2.

8. A compound of formula I according to claim 2, wherein
R_1 is CF_3;
R_2 is C_1-C_3alkyl or C_1-C_3alkoxy-C_1-C_3alkyl;
R_3 is hydrogen or fluoro;
Q is Q1;
R_4 is C_6-C_{10}bicycloalkyl unsubstituted or substituted by methyl, ethyl or CF_3;
C_6-C_{10}bicycloalkenyl unsubstituted or substituted by methyl, ethyl or CF_3;
C_6-C_{10}bicycloalkadienyl unsubstituted or substituted by methyl, ethyl or CF_3; a group of the form



wherein R_7, R_8 and R_9 are independently of each other C_1-C_3alkyl or
C_1-C_3haloalkyl; or a group

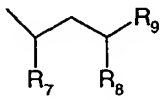


wherein R_{10} and R_{11} are independently of each other hydrogen or
halogen and n = 1 or 2; and
R_5 and R_6 are independently of each other hydrogen, chloro or fluoro.

9. A compound of formula I according to claim 8, wherein

R_2 is methyl or CH_2OCH_3;

R_4 is a group of the form



wherein R_7, R_8 and R_9 are independently of each other CF_3, methyl or ethyl, preferably methyl; and

R_5 and R_6 are independently of each other hydrogen, fluoro or chloro.

10. A compound of formula I according to claim 9, wherein

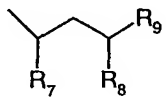
R_2 is methyl.

11. A compound of formula I according to claim 9, wherein

R_2 is methyl;

R_3 is hydrogen;

R_4 is a group of the form



wherein R_7, R_8 and R_9 are independently of each other methyl or ethyl, preferably methyl; and

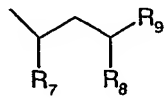
R_5 and R_6 are independently of each other hydrogen, fluoro or chloro.

12. A compound of formula I according to claim 9, wherein

R_2 is methyl;

R_3 is fluoro;

R_4 is a group of the form



wherein R_7, R_8 and R_9 are independently of each other methyl or ethyl, preferably methyl; and

R_5 and R_6 are independently of each other hydrogen, fluoro or chloro.

13. A compound of formula I according to claim 1, wherein

R_1 is CF_2H or CFH_2;

R_2 is C_1-C_3alkyl, C_1-C_3haloalkyl or C_1-C_3alkoxy-C_1-C_3alkyl;

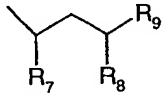
R_3 is hydrogen or fluoro;

Q is Q1;

R_4 is C_6-C_{10}bicycloalkyl unsubstituted or substituted by methyl, ethyl or CF_3;

C_6-C_{10}bicycloalkenyl unsubstituted or substituted by methyl, ethyl or CF_3;

C_6-C_{10}bicycloalkadienyl unsubstituted or substituted by methyl, ethyl or CF_3; a group of the form



wherein R_7, R_8 and R_9 are independently of each other C_1-C_3alkyl or

C_1-C_3haloalkyl; and

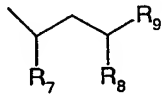
R_5 and R_6 are independently of each other hydrogen, chloro or fluoro.

14. A compound of formula I according to claim 13, wherein

X is oxygen;

R_2 is methyl or CH_2OCH_3;

R_4 is a group of the form



wherein R_7, R_8 and R_9 are independently of each other C_1-C_3alkyl or

C_1-C_3haloalkyl.

15.A compound of formula I according to claim 1, wherein

R_1 is CF_2H or CFH_2;

R_2 is C_1-C_3alkyl, C_1-C_3haloalkyl or C_1-C_3alkoxy-C_1-C_3alkyl;

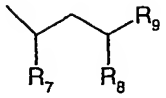
R_3 is hydrogen or fluoro;

Q is Q2, Q3 or Q4;

R_4 is C_6-C_{10}bicycloalkyl unsubstituted or substituted by methyl, ethyl or CF_3;

C_6-C_{10}bicycloalkenyl unsubstituted or substituted by methyl, ethyl or CF_3;

C_6-C_{10}bicycloalkadienyl unsubstituted or substituted by methyl, ethyl or CF_3; a group of the form



wherein R_7, R_8 and R_9 are independently of each other C_1-C_3alkyl or C_1-C_3haloalkyl; and

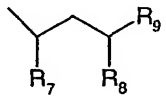
R_5 and R_6 are independently of each other hydrogen, chloro or fluoro.

16. A compound of formula I according to claim 15, wherein

X is oxygen;

R_2 is methyl or CH_2OCH_3;

R_4 is a group of the form



wherein R_7, R_8 and R_9 are independently of each other C_1-C_3alkyl or C_1-C_3haloalkyl.

17. A compound of formula I according to claim 1 selected from

1-methyl-4-trifluoromethyl-1H-pyrrole-3-carboxylic acid [2-(1,3-dimethylbutyl)phenyl]amide;

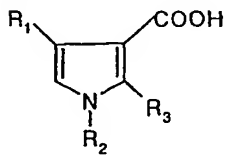
1-methoxymethyl-4-trifluoromethyl-1H-pyrrole-3-carboxylic acid [2-(1,3-dimethylbutyl)phenyl]amide;

1-methyl-2-fluoro-4-trifluoromethyl-1H-pyrrole-3-carboxylic acid [2-(1,3-dimethylbutyl)phenyl]amide;

1-methoxymethyl-2-fluoro-4-trifluoromethyl-1H-pyrrole-3-carboxylic acid [2-(1,3-dimethylbutyl)phenyl]amide;

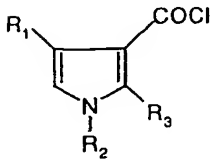
1-methyl-4-trifluoromethyl-1H-pyrrole-3-carbothioic acid [2-(1,3-dimethylbutyl)phenyl]amide.

18. A process for the preparation of compounds of formula I, which comprises in a first step preparing the compounds of formula I wherein X=O by converting the pyrrolecarboxylic acid II



II

to the acid chloride III



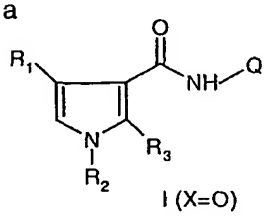
III

and by reacting the pyrrole acid chloride III with the amine IV

H_2N-Q IV

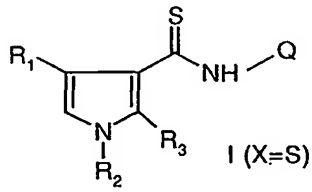
to the compounds of formula I

a



I (X=O)

and optionally converting these compounds to the compounds of formula I wherein X=S by reacting with Lawesson-Reagent or P_2S_5 in dioxane, tetrahydrofurane or toluene at a temperature of 0° - reflux to



I (X=S)

and wherein R_1, R_2, R_3 and Q are as defined for formula I in claim 1.

19. A composition for controlling microorganisms and preventing attack and infestation of plants, wherein the active ingredient is a compound as claimed in claim 1 together with a suitable carrier.

20. Use of a compound of formula I according to claim 1 for protecting plants against infestation by phytopathogenic microorganisms.

21. A method of controlling or preventing infestation of cultivated plants by phytopathogenic microorganisms by application of a compound of formula I as claimed in claim 1 to plants, to parts thereof or the locus thereof.

22. The amine intermediates of formula IV H_2N-Q
wherein Q and R_4, R_5, R_6, R_7, R_8, R_9, R_{10} and R_{11} are as defined in claim 1.

23. A compound of formula IV according to claim 22 selected from
2-bicyclo[2.2.2]oct-2-yl-phenylamine;
2-bicyclo[2.2.2]oct-2-en-2-yl-phenylamine;
2-bicyclo[2.2.2]octa-2,5-dien-2-yl-phenylamine;
2-(2-aminophenyl)-1,1,1-trifluoromethyl-4-methyl-pentan-2-ol;
2-(2-aminophenyl)-1-cyclopropyl-propan-2-ol;
2-(2-aminophenyl)-1-cyclopropyl-butan-2-ol;
2-(3-methyl-1-trifluoromethyl-but-1-enyl)-phenylamine;
2-(3-methyl-1-trifluoromethyl-butyl)phenylamine;
2-(2-cyclopropyl-1-methyl-ethyl)phenylamine; and
2-(1-cyclopropylmethyl-propyl)phenylamine.

24. A process for the preparation of compounds of the formula IV according to claim 22, characterized by
Route a) reacting the formyl derivate W-NHCHO of formula X with a ketone of formula IX in the presence of 2-3 equivalents of n-BuLi or sec-BuLi or another strong base in a solvent at a temperature of –100 to –110°C providing the compounds of formula XI (WY-NHCHO); converting the formyl derivative of formula XI to the amine compounds of formula VI (H_2N-WY) in a basic hydrolysis by reacting with NaOH or KOH in alcohols; and hydrogenation the amine VI to the compounds IV (H_2N-Q) with Pd/charcoal in the presence of a strong acid (f.e. sulfuric acid) or alternatively elimination of water and than hydrogenation; or
Route b) reacting the amine of formula XII (H_2N-T) with an excess of the Grignard reagent of formula XV in a solvent like THF or ether at a temperature 0°C to reflux to the amine of formula VI; and

converting the amine VI to the amine XIV (H_2N-TG) by elimination of water; the hydrogenation of XIV with Pd or Pt on charcoal in a solvent like THF or alcohols at temperatures of 0°C to reflux provides the compounds of formula IV; or directly the compounds of formula VI by hydrogenation with Pd on charcoal in the presence of sulfuric acid in a solvent like an alcohol provides the amines IV; or

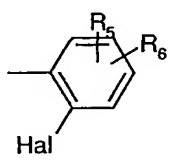
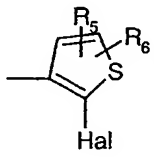
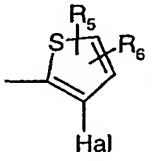
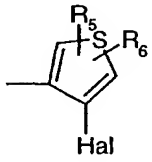
Route c) reacting the nitro derivative NO_2-W (formula XIII) with a ketone of formula IX providing the nitro derivative NO_2-WY of formula VII;

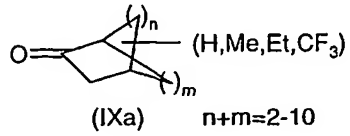
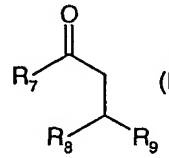
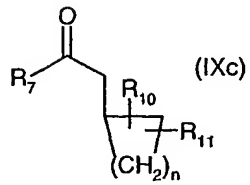
transforming the compound of formula VII by reaction with $SOCl_2$ or $POCl_3$ in pyridine at a temperature of 0°C to reflux to the derivative VIII (NO_2-TG); and

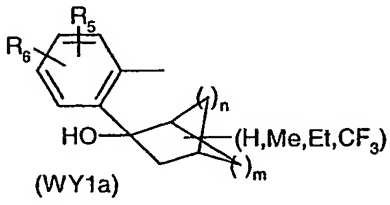
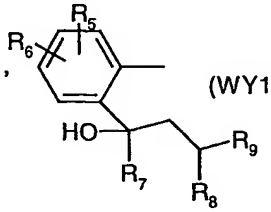
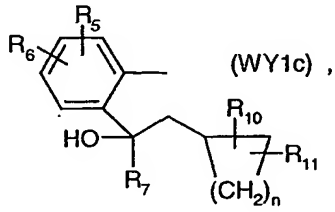
hydrogenation of the compound of formula VIII with Raney-Ni in alcohol at a pressure of 50-200 bar and a temperature of 50-150°C to the compound of formula IV;

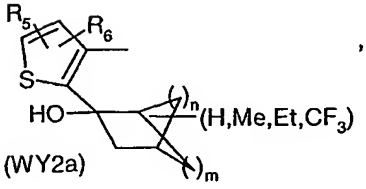
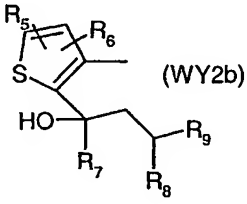
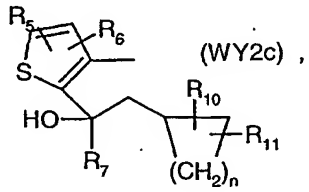
wherein Q, R_5, R_6, R_7, R_8, R_9, R_{10}, R_{11} are as defined in claim 1 for compounds of the formula I, Hal is Br or I and

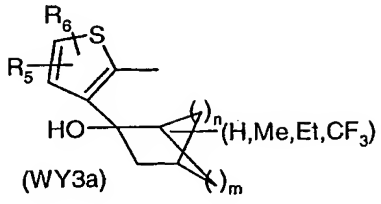
wherein

W is  (W1),  (W2),  (W3) or  (W4)

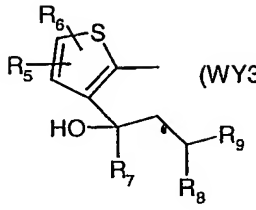
IX is  (IXa) n+m=2-10,  (IXb) or  (IXc)

WY is  (WY1a),  (WY1b),  (WY1c),

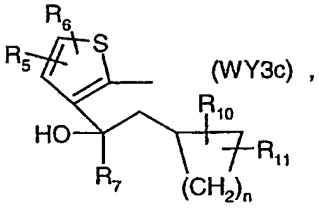
 (WY2a),  (WY2b),  (WY2c),



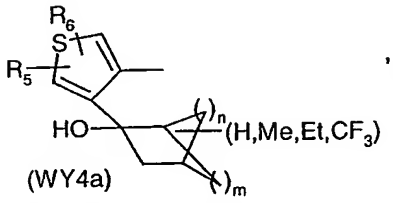
(WY3a)



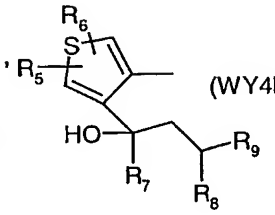
(WY3b)



(WY3c),



(WY4a)



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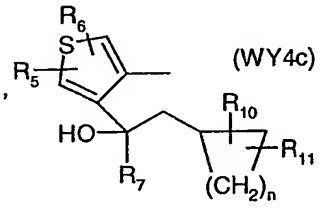
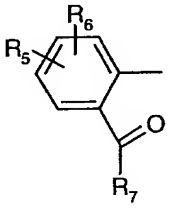
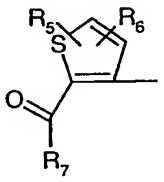
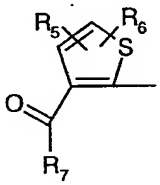


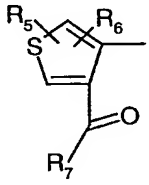
(WY4c),

and wherein n+m=2-10

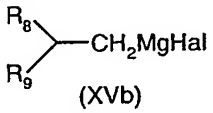
T is 

(T1), 

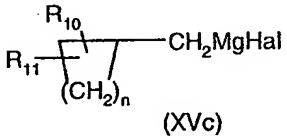
(T2), 

(T3) or 

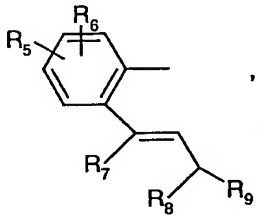
(T4)

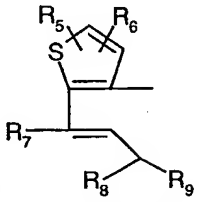
XV is 

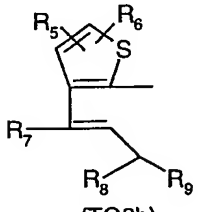
(XVb)

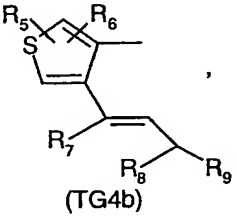
or 

(XVc)

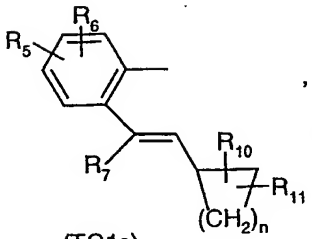
TG is 

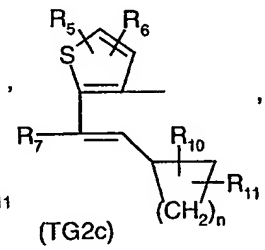
(TG1b), 

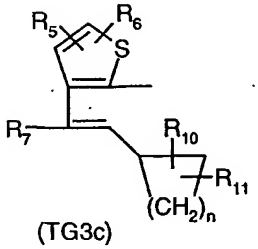
(TG2b), 

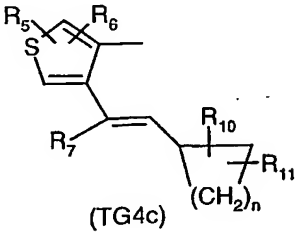
(TG3b), 

(TG4b)



(TG1c), 

(TG2c), 

(TG3c), 

(TG4c)

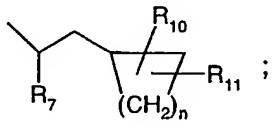
25. A process according to claim 24, Route a), for compounds of formula IV wherein

Q is Q1; and

R_4 is C_7-C_9bicycloalkyl unsubstituted or substituted by methyl or CF_3;

C_7-C_9bicycloalkenyl unsubstituted or substituted by methyl or CF_3;

C_7-C_9bicycloalkadienyl unsubstituted or substituted by methyl or CF_3; or a group



;

R_5 and R_6 are hydrogen; and wherein R_7, R_{10}, R_{11} and n are as defined in claim 1.

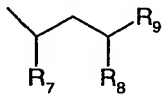
26. A process according to claim 24, Route a), wherein

Q is Q2, Q3 or Q4; and

R_4 is C_7-C_{10}bicycloalkyl unsubstituted or substituted by methyl or CF_3;

C_7-C_{10}bicycloalkenyl unsubstituted or substituted by methyl or CF_3;

C_7-C_{10}bicycloalkadienyl unsubstituted or substituted by methyl or CF_3; or a group



;

R_5 and R_6 are hydrogen; and wherein R_7, R_8, R_9 and n are as defined in claim 1.

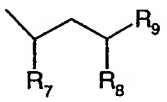
27. A process according to claim 24, Route b), wherein

Q is Q1; and

R_4 is C_7-C_{10}bicycloalkyl unsubstituted or substituted by methyl or CF_3;

C_7-C_{10}bicycloalkenyl unsubstituted or substituted by methyl or CF_3;

C_7-C_{10}bicycloalkadienyl unsubstituted or substituted by methyl or CF_3;

or a group 

;

R_5 and R_6 are hydrogen; and wherein R_7, R_8, R_9 and n are as defined in claim 1.

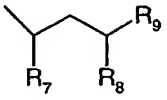
28. A process according to claim 24; Route b), wherein

Q is Q2, Q3 or Q4; and

R_4 is C_7-C_{10}bicycloalkyl unsubstituted or substituted by methyl or CF_3;

C_7-C_{10}bicycloalkenyl unsubstituted or substituted by methyl or CF_3;

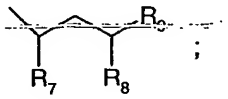
C_7-C_{10}bicycloalkadienyl unsubstituted or substituted by methyl or CF_3;

or a group  ;

R_5 and R_6 are hydrogen; and wherein R_7, R_8, R_9 and n are as defined in claim 1.

29. A process according to claim 24, Route c), wherein

Q is Q1; and

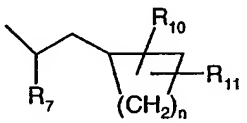
R_4 is a group  ;

R_5 and R_6 are hydrogen;

R_7 is CF_3; and wherein R_8, R_9 and n are as described in claim 1.

30. A process according to claim 24, Route c), wherein

Q is Q1;

R_4 is a group  ;

R_5 and R_6 are hydrogen;

n is 1;

R_7 is CF_3; and wherein R_{10} and R_{11} are as defined in claim 1.

INTERNATIONAL SEARCH REPORT

International Application No
.../EP 01/12830

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07D207/327 C07D409/12 C07D207/32 A01N43/36 C07C211/46

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07D C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, CHEM ABS Data, WPI Data, BEILSTEIN Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00 09482 A (NOVARTIS ERFIND VERWALT GMBH ;EBERLE MARTIN (CH); NOVARTIS AG (CH)) 24 February 2000 (2000-02-24) page 1 -page 3; claim 1 ---	1-21
A	EP 0 737 682 A (MITSUI TOATSU CHEMICALS) 16 October 1996 (1996-10-16) page 2, line 35 -page 3, line 29; claim 1 ---	1-21
A	EP 0 841 336 A (MITSUI TOATSU CHEMICALS) 13 May 1998 (1998-05-13) page 2, line 10 -page 3, line 29; claim 1 ---	1-21
A	EP 0 824 099 A (MITSUI TOATSU CHEMICALS) 18 February 1998 (1998-02-18) page 4, line 5 -page 5, line 12; claim 1 ---	1-21
	-/--	

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
6 February 2002	22 04 02

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Usuelli, A

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INTERNATIONAL SEARCH REPORT

International Application No
/EP 01/12830

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	WO 01 49664 A (WALTER HARALD ;SYNGENTA PARTICIPATIONS AG (CH); SCHNEIDER HERMANN) 12 July 2001 (2001-07-12) page 1 -page 11; claim 1; tables 1,2 -----	1-21

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

national application No.
PCT/EP 01/12830

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-21

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-21

   Compounds of formula (I)

2. Claims: 22 (part)- 24(part), 25, 27, 29, 30

   Intermediates of formula (IV) in which Q is Q1

3. Claims: 22(part)-24(part), 26,28

   Intermediates of formula (IV) in which Q is Q2, Q3 or Q4

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
EP 01/12830

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
WO 0009482	A	24-02-2000	AU	5513899 A	06-03-2000
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			DE	69618370 D1	14-02-2002
			EP	0737682 A1	16-10-1996
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			KR	269420 B1	16-10-2000
			US	5869427 A	09-02-1999
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			CN	1338452 A	06-03-2002
			CN	1178791 A ,B	15-04-1998
			DE	69708004 D1	13-12-2001
			EP	0824099 A1	18-02-1998
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			JP	10310577 A	24-11-1998
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